ACADEMIC'S LILIPUT SERIES

CHEMISTRY FORMULAE

ACADEMIC'S

CHEMISTRY FORMULAE

For students of NCERT, CBSE
and all regional boards of
A.P., U.P., T.N., and M.P. boards.
Also useful for IIT, PMT, NTSE, NDA
and other competitive exams.

By

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AUTHOR'S NOTE

This liliput book is an attempt to present the subject in a simple and concise manner. It has been specially prepared according to the syllabus of U.P. Board, CBSE and NCERT.

One of the aims of the present book is to provide maximum terms and definitions of the subject in minimum possible and understandable language. The book will be of immense utility to those students who are going to appear various objective type entrance and competitive examinations. The book will also be useful in revising the subject quickly.

Help and cooperation of readers will encourage us to improve and amend this book. Your valuable constructive suggestions regarding the betterment of the book will be our pleasure and are warmly solicited.

Dr. U.N. Shukla

Academic's

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PART – I

Physical Chemistry

Matter And its Properties

Matter : Something which occupies space and carries mass is known as matter e.g. air, water, steel, wood, gold etc.

Mass (m) : The quantity of matter present in a body is known as mass.

Units of mass : Mass is usually expressed in Kilogram (Kg), gram (g), milligram (mg) or microgram (μg)

$$1 \text{ kilogram} = 1000 \text{ g or } 1 \times 10^3 \text{ g.}$$

$$1 \text{ g} = 1000 \text{ mg or } 1 \times 10^3 \text{ mg.}$$

$$1\ g = 1000000\ \mu g$$

$$\text{or } 1 \times 10^6\ \mu g.$$

Volume (v) : The space occupied by a body is known as its volume.

Units of volume : Volume is expressed in metre^3, dm^3, cm^3, mm^3.

$$1 \text{ metre} = 10 \text{ dm}$$

$$1 \text{ m}^3 = 10^3 \text{ dm}^3$$

$$1 \text{ metre} = 100 \text{ cm}$$

$$1 \text{ m}^3 = 100^3 \text{ cm}^3 = 10^6 \text{ cm}^3$$

$$1 \text{ metre} = 1000 \text{ mm}$$

$$1 \text{ m}^3 = 1000^3 \text{ mm}^3 = 10^9 \text{ mm}^3$$

Density (d) : Mass of unit volume is called density which is mathematically expressed as the ratio of mass to volume.

$$\text{density (d)} = \frac{\text{mass (m)}}{\text{volume (v)}}$$

States of matter : Matter exists in three different states i.e. solid, liquid and gas.

Solid : Solid has a definite shape and a definite volume. e.g. book, chair, copper, wood etc.

Liquid : Liquid has a definite volume but not a definite shape. It takes the shape of container. e.g. water, milk etc.

Gas : Gas neither has a definite shape nor has a definite volume. It takes the shape of container and fills it completely. e.g. oxygen, nitrogen, air etc.

Change in State : Solids can be changed into liquids and gases and vice versa. This change of state from one state of matter to another takes place under following conditions.

During the course of change of state

(i) The temperature remains constant and is a physical characteristic of every substance.

(ii) The amounts of energy spent during direct changes are equal to those released in inverse changes.

Comparison of Forces in three States of Matter

Solid	*Liquid*	*Gas*
The molecules are held very firmly to one another by strong intermolecular forces of attraction so they acquire a definite shape and definite volume.	The molecules are held up less firmly than in solids. This makes them to slide over one another easily and thus they take the shape of the container.	The intermolecular forces of attraction are least in gases. This is because of their large intermolecular spacing. So gaseous molecules are free to move in any direction with any velocity. Thus gases can assume the shape and volume of container very easily.

$$\text{Solid} + \text{heat } (q_1) \longrightarrow \text{liquid}$$

$$\text{liquid} \longrightarrow \text{solid} + \text{heat } (q_2)$$

then $q_1 = q_2$, if the same quantities are involved.

The energy expended or released is indicated as **latent heat** and is expressed in J $mole^{-1}$.

Latent heat : It is the amount of heat absorbed or evolved when one mole of a substance changes from one state to another at a constant temperature. It is expressed in J $mole^{-1}$.

Latent heat of fusion : It is the amount of heat absorbed when one mole of a solid changes into liquid at constant temperature (melting point). The latent heat of fusion of ice is 80 Kcal/mole.

Latent heat of vaporisation : It is the amount of heat absorbed when one mole of a liquid is changed to gaseous state at constant temperature (boiling point). The latent

heat of vaporisation of water is 536 Kcal/mole.

Fusion : A process in which solid changes to liquid.

$$\text{Solid} \longrightarrow \text{liquid}$$

Vaporisation : A process in which a liquid changes to gas.

$$\text{Liquid} \longrightarrow \text{Gas}$$

Sublimation : It is a process in which a solid changes directly into the gaseous state without going through the liquid state.

$$\text{Solid} \longrightarrow \text{Gas}$$

The substances having this property are known as sublime substances e.g. NH_4Cl (ammonium chloride), I_2 (Iodine), Benzoic acid etc.

Liquifaction : It is the process which involves the change of a gas into the liquid state.

Solidification : It is the process which involves the change from liquid to solid state.

Classification of Matter :

The matter can be classified into three main classes : (i) Elements, (ii) Mixtures, (iii) Compounds.

Element : An element is a substance which cannot be split up into two or more simpler substances by any of the physical or chemical methods e.g. hydrogen, oxygen, sodium, iron, silver etc.

Mixture : A mixture is a substance which consists of two or more elements or compounds not chemically combined together in indefinite proportions e.g. air (a mixture of oxygen, nitrogen inert gases, hydrogen etc.).

Compound : A compound is a substance consisting of two or more elements in a fixed ratio which are chemically combined together e.g. water (H_2O), Sodium Chloride (NaCl) etc.

Structure of Atom : Basic constituents:

Proton : It is a positively charged particle present into the nucleus of an atom. The

charge of proton is 1.6×10^{-19} coulombs and the mass of a proton is 1.672×10^{-24} g.

Electron : Electron is a negatively charged particle that evolves around the nucleus in fixed orbits (energy levels). The charge of an electron is 1.6×10^{-19} coulombs and the mass of the electron is 9.1×10^{-28} g.

Neutron : It is an electrically neutral particle present in the nucleus of an atom. The mass of neutron is 1.675×10^{-24} g.

Atomic Number : Atomic number of an element is the number of protons present in the nucleus of the atom of that element.

Atomic Number = Number of protons = Number of electrons.

Mass Number : It is equal to the total number of protons and neutrons (i.e. nucleous) present in the atom of an element.

Mass Number = Number of protons

\+ Number of neutrons

= Number of Nucleous

Isotopes : Atoms of the same element having same atomic number but different atomic weights (mass numbers) are known as isotopes e.g. $^{37}_{17}Cl$, $^{36}_{17}Cl$ and $^{35}_{17}Cl$ are the three isotopes of chlorine.

Isobars : Atoms of different elements having same atomic weight (mass number) but different atomic numbers are known as isobars e.g. K-40 and Ar-40.

DIFFERENT MODELS OF ATOM

Rutherford's Model of Atom : According to this model proposed by Rutherford in 1912, an atom consists of a positively charged central portion which is known as nucleus. It is surrounded by electrons. The number of protons in the nucleus is equal to the number of electrons surrounding it. Hence, atom is electrically neutral.

All the mass of the atom is concentrated in the nucleus of the atom. The volume of nucleus is very small as compared to total

volume of the atom. The nucleus and electrons are held together by electrostatic forces of attraction. This model was based on the experiments of Rutherford.

Bohr's Model of Atom : Niels Bohr proposed this model in 1913. He slightly modified the Rutherford's model to overcome its limitations. According to this model :

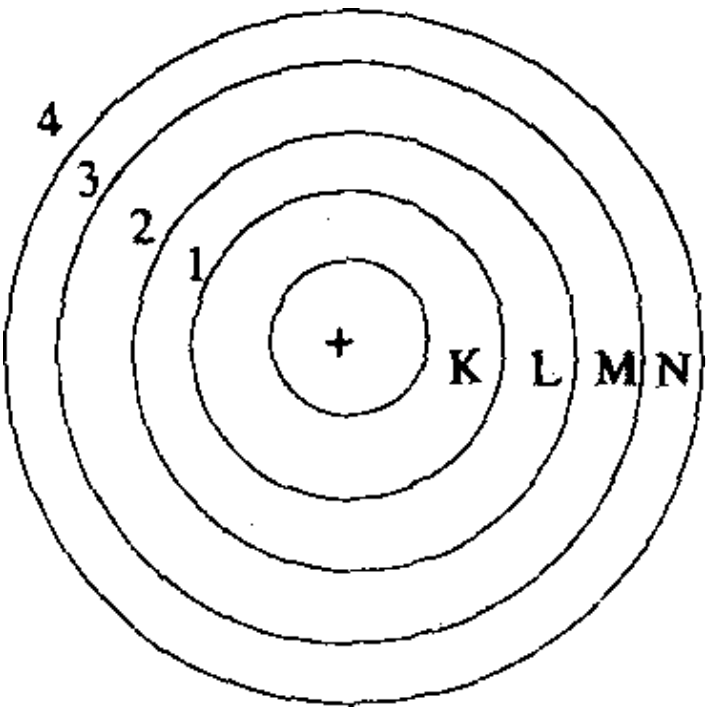
(i) An atom consists of a small positively charged nucleus situated at its centre.

(ii) The negatively charged electrons revolve around the nucleus in certain definite circular paths called energy levels.

(iii) Each energy level is associated with a definite amount of energy.

(iv) The energy levels are either numbered $n = 1, 2, 3, 4 \ldots$ etc. or designated as K, L, M, N etc. outwards from the nucleus.

(v) The change in energy of an electron takes place only when it jumps from



lower energy level to higher energy level (gain of energy) or when it jumps from a higher energy level to a lower energy level (loss of energy). This means that as long as the electrons remain in a given energy level, they neither gain nor lose energy and atom remains stable.

Dual Nature of Electrons : According to De Broglie, all material particles like

electrons, protons, neutrons, atoms and molecules exhibit dual character.

De Broglie's Relationship : He gave the following relationship between wavelength (λ) and momentum (p) of a particle.

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \frac{h}{p}$$

where λ = wavelength of the particle

m = mass of the particle

v = velocity of the particle

p = momentum of the particle

h = Planck's constant (6.626×10^{34} JS) or 6.626×10^{-34} kg $m^2 s^{-1}$)

Velocity of Radiations : Mathematically it can be expressed as

$$v = f \times \lambda$$

where, v = velocity of all types of electromagnetic radiations

f = frequency of radiations.

λ = wavelength of radiations.

Velocity of all types of electromagnetic radiations is equal to 3×10^{-8} m/s.

Wave Number : The reciprocal of wavelength (λ) is known as wave number. Mathematically, wave number $\nu = 1 / \lambda = \nu / c$

or $$\bar{\nu} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where n_1 and n_2 are integers such that $n_2 > n_1$, R is known as Rydberg constant for hydrogen.

Energy of Proton : $E = h\nu = h\frac{c}{\lambda} = hc\nu$

where E = energy of proton

h = Planck's constant

= 6.625×10^{-34} joule seconds.

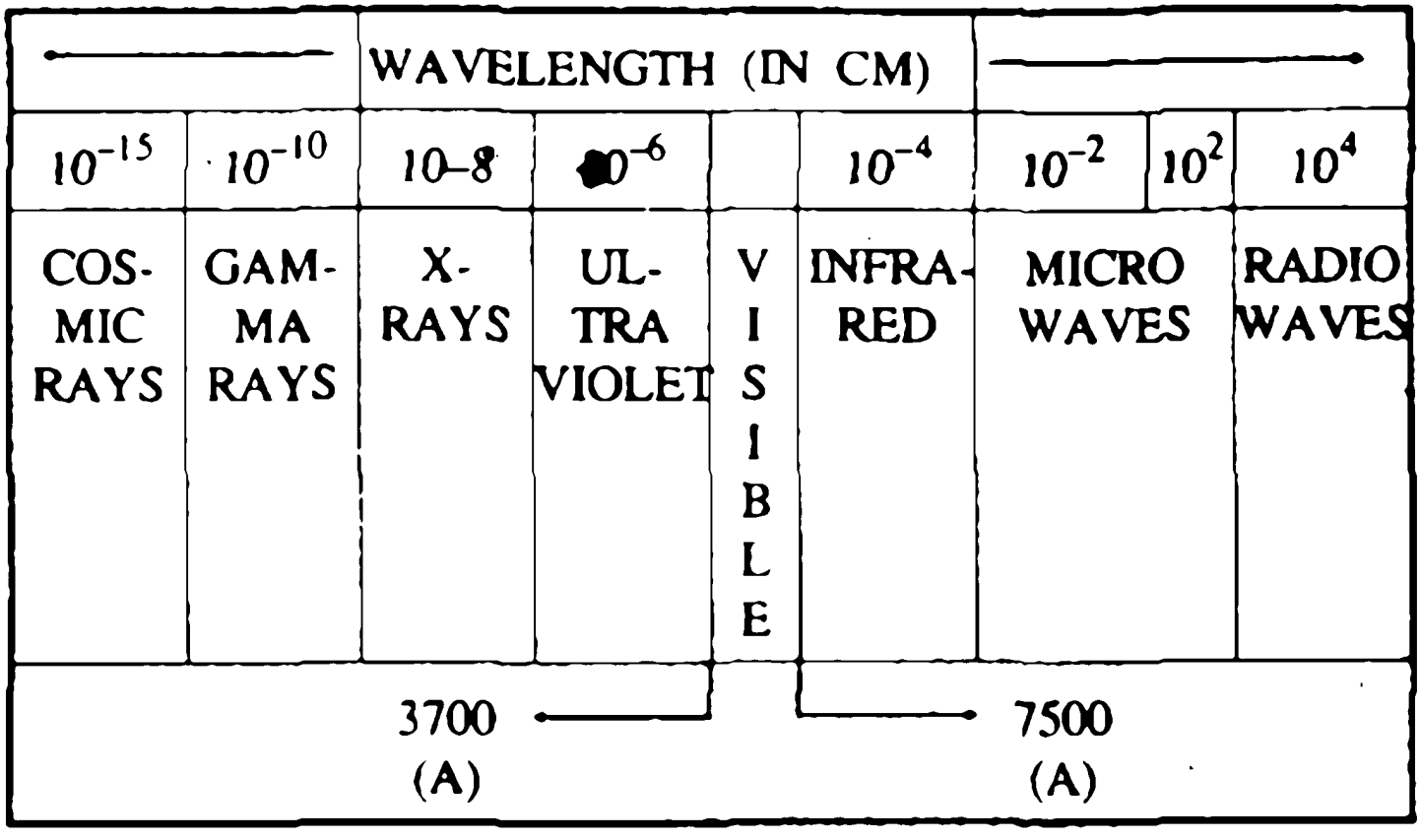
Electromagnetic Waves : Maxwell proposed that light and other forms of radiant energy propagate through space in the form of waves. These waves have electric and magnetic fields associated with them and are called electromagnetic waves (radiations). All types of electromagnetic radiations travel with the same speed 2.998 $\times 10^8$ m/s (approximately 3×10^8 m/s) and do not require any medium for their propagation. However the different types of waves differ in their wavelength and so in their frequency.

Electromagnetic Spectrum : The arrangement of different types of electromagnetic radiations in order of their increasing wavelengths or decreasing frequencies is called as electromagnetic spectrum.

VISIBLE SPECTRUM

V	I	B	G	Y	O	R

Here V stands for VIOLET


WAVELENGTH (IN CM)
10^{-15}
10^{-10}
10–8
10^{-6}
10^{-4}
10^{-2}
10^{2}
10^{4}
COS-MIC RAYS
GAM-MA RAYS
X-RAYS
UL-TRA VIOLET
VISIBLE
INFRA-RED
MICRO WAVES
RADIO WAVES
3700 (A)
7500 (A)

I	stands for	INDIGO
B	stands for	BLUE
G	stands for	GREEN
Y	stands for	YELLOW
O	stands for	ORANGE
R	stands for	RED

The complete electromagnetic spectrum is shown in the figure below. Different regions of the spectrum are identified by different names.

Bohr Model for the Hydrogen Atom :

The electron moves in circular orbits (stationary states) without irradiating energy. Permitted orbits have an angular momentum:

$$l = n \frac{h}{2\pi}$$

h —→ PLANCK'S constant ;

$n \longrightarrow 1, 2, 3 \ldots$ PRINCIPAL QUANTUM NUMBER

The emission and absorption of electromagnetic waves occurs only when transitions take up between two stationary states and the frequency of the radiation emitted or absorbed is expressed by :

$$hf = E_n - E_{n'} \quad \text{here} \quad n > n'$$

E_n, $E_{n'}$ are the energies of the stationary states characterised by the principal quantum numbers n and n'.

$$r_n = \frac{h^2 \varepsilon_0}{\pi m_e e^2} n^2$$

r_n = radii of the permitted orbits.

$\varepsilon_0 = 8.85 \times 10^{-12}$ F.m $\rightarrow$
Permitivity of free space.

$m_e = 9.11 \times 10^{-11}$ kg $\rightarrow$
rest mass of electrons.

$e = 1.602 \times 10^{-19}$ coulombs $\rightarrow$ electron charge

$$E_n = -\frac{M_e \cdot e^4}{\varepsilon_0^2 \cdot h^2} \cdot \frac{1}{n^2}$$

$E_n \longrightarrow$ Energy of the permitted stationary states.

$$f = \frac{M_e \cdot e^4}{8\,\varepsilon_0^2 \cdot h^3}\left[\frac{1}{n^2} - \frac{1}{n'^2}\right]$$

$$= CR_H\left[\frac{1}{n^2} - \frac{1}{n'^2}\right], \quad n' > n$$

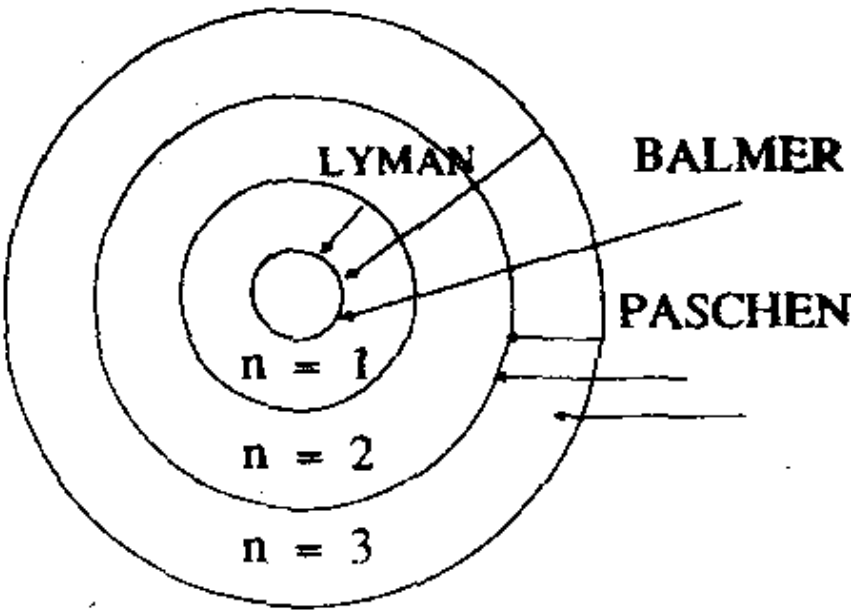
$f \rightarrow$ frequencies emitted or absorbed by the hydrogen atom.

$n, n' \rightarrow$ Principal quantum numbers of the stationary states between which transition takes place.

$C \longrightarrow$ Speed of light

$R_H \longrightarrow$ RYDBERG'S constant for hydrogen $= 1.097 \times 10^7\ m^{-1}$.

Emission Spectrum of Hydrogen :



$n = 1$; $n' = 2, 3 \ldots$ LYMAN'S Series

$n = 2$; $n' = 3, 4 \ldots$ BALMER'S Series

$n = 3$; $n' = 4, 5 \ldots$ PASCHEN'S Series

$n = 4$; $n' = 5, 6 \ldots$ BRACKETT'S Series

$n = 5$; $n' = 6, 7 \ldots$ PFUND'S Series

The Balmer Formula : Wavelength of the visible lines in the atomic spectrum of hydrogen follows the following formula :

$$\bar{\nu} = \frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{n^2}\right], \quad n = 3, 4, 5, \ldots$$

where $\bar{\nu}$ is the wave number

R_H= Rydberg's constant
(= $1.097 \times 10^7 m^{-1}$) for hydrogen.

Rydberg Formula : Balmer formula was generalised to account for new sets of spectral lines of hydrogen atom.

$$1/\lambda = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ where } n_2 > n_1$$

This is known as Rydberg's equation.

Heisenberg's Uncertainty Principle : It is impossible to determine simultaneously both the position and momentum of an electron with accuracy Mathematically

$$\Delta x \cdot \Delta p \geq \frac{h}{2\pi}$$

where Δx and Δp are the errors in the determination of position and momentum of an electron.

Orbital : It is defined as three dimensional space around the nucleus of an atom where there in maximum probability of finding an electron. It is different from orbit which is a well defined path around the nucleus in which the electron revolves. Orbital is the sublevel of orbit.

Quantum Numbers : There are four quantum numbers to define the state of an electron around the nucleus of an atom. They are as follows :

(i) **Principal Quantum Number** (n) : It gives the rough idea about the location and energy of an electron. It can have any integral value except zero. It also provides the average distance of electron from the nucleus. The energy level nearest to the nucleus is $n=1$ and is called K-orbit or Ist shell (orbit). The energy of electron

increases with the increase in the value of n.

(ii) Azimuthal Quantum Number (l) : This quantum number determines the shape of the electron orbit. This denotes the sub-energy level or sub-shell present into a given main energy level (shell or orbit) to which the concerned electron belongs.

It determines the energy associated with the angular momentum of the electron It (l) has integral values from 0 to ($n - 1$) where n is the principal quantum number. It is related to the shape of the electron cloud (orbital). The eccentricity of the ellipse can be found from the relation $\frac{b}{a} = \frac{l+1}{n}$.

This quantum number is also known as secondary or subsidiary quantum number.

Magnetic Quantum Number (m) : This quantum number describes the different orientations of the orbital (electron cloud) in *space under the influence of a magnetic* field. It has integral values from $-l$ . . . 0

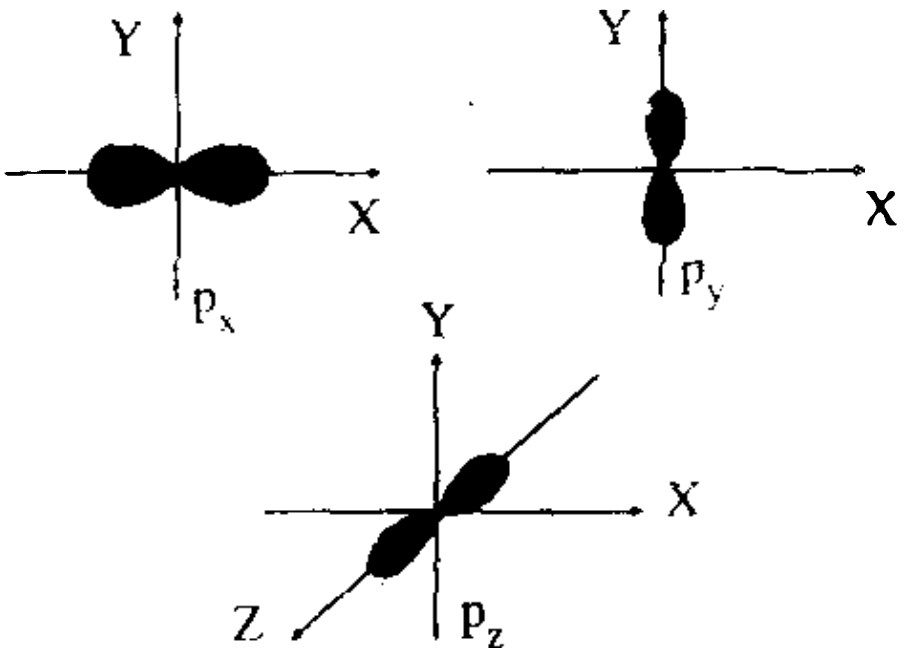
. . . $+l$ for any particular value of azimuthal quantum number. Thus, it has a total of $(2l+1)$ values for a given value of l.

Spin Quantum Number (s) : It gives an idea about the spin of the electron. An electron can spin in two possible ways (clockwise or anticlockwise), accordingly spin quantum number can have only two values $+\frac{1}{2}$ or $-\frac{1}{2}$.

Shape of *s*-orbital : For s-orbital the value of azimuthal quantum number (l) is zero (0) and therefore magnetic quantum number (m) can have only one value i.e. $m = 0$. So the possibility of finding the electron is same in all directions from the nucleus. The shape of s-orbital is spherical.

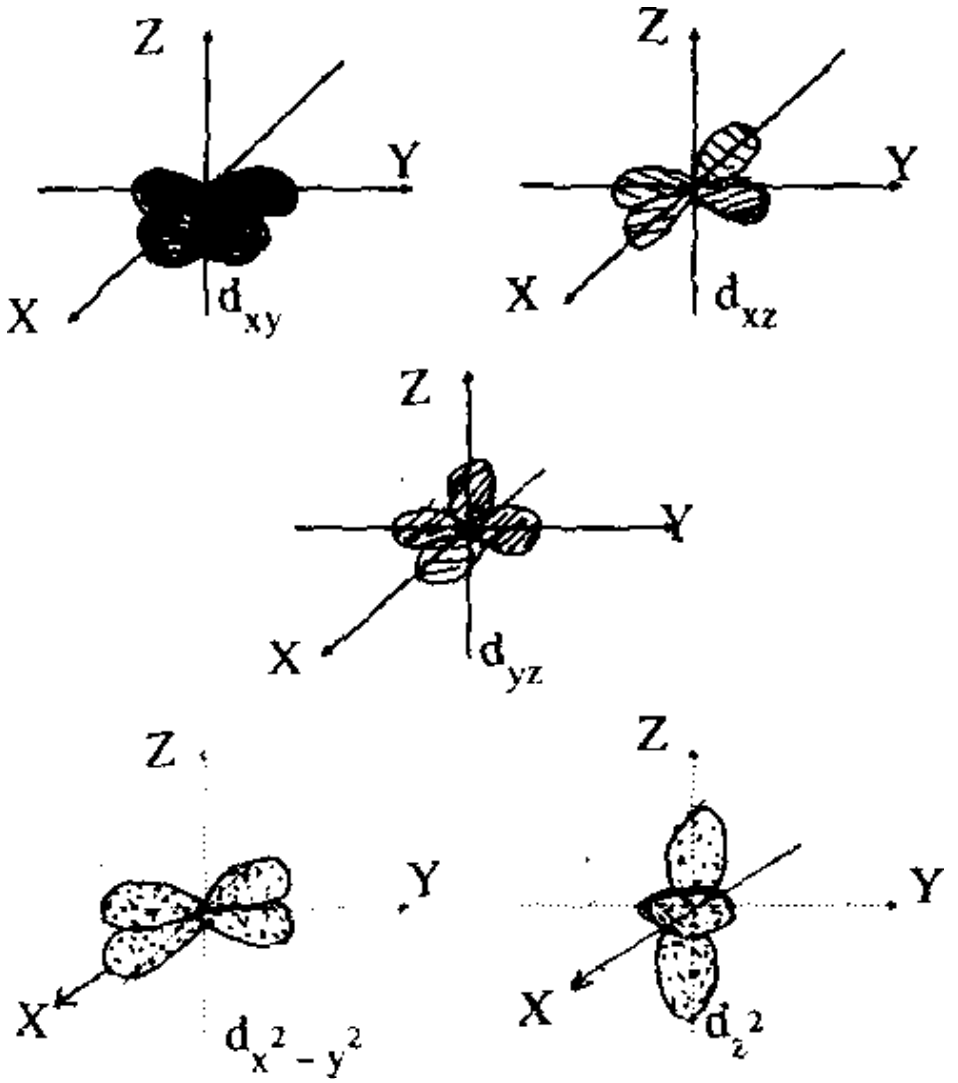
Node : In between two spheres ($1s$ and $2s$ or $2s$ and $3s$) there is a region where the electron density is zero. This is known as Node

Shape of *p*-orbital : For p-orbital, the value of $l = 1$. There are three possible



orientations corresponding to three value of *m* i.e. −1, 0 and +1. These are oriented along the three mutually right angled axes i.e. *X*, *Y* and *Z*. Each orbital consists of two lobes, one on each side of the nucleus along a particular axis. These two lobes are separated by a node i.e. by a plane of zero electron density.

Shape of *d*-orbital : For *d*-orbital, the value of $l = 2$. There are five values of *m* i.e. −2, −1, 0, +1, +2 and consequently there are five orientations of *d*-orbital as shown below :



Schrodinger wave equation : To describe the wave motion of an electron, Schrodinger gave the following mathematical equation. This equation deals with the wave equation of a single electron.

$$\frac{\delta^2\psi}{dx^2} + \frac{\delta^2\psi}{dy^2} + \frac{\delta^2\psi}{dz^2} + \frac{8\pi^2 m}{h}(E - V)\psi = 0$$

where x, y and z are the three space coordinates.

m is the mass of the electron

h is Planck's constant

E is total energy.

V is the potential energy of the electron.

ψ is the amplitude of the electron wave.

$\frac{\delta^2\psi}{dx^2}, \frac{\delta^2\psi}{dy^2}, \frac{\delta^2\psi}{dz^2}$ represent the second derivatives of ψ along x, y and z axis.

Arrangement of electrons in the atom : The arrangement of electrons in different shells or energy levels of an atom is known as electronic configuration. The maximum number of electrons which can be put in a particular shell was given by Bohr and Bury. According to this, the maximum number of

electrons that can be accommodated in any of the energy levels is given by $2n^2$ where n is the number of that energy level. The number of electrons that can be accommodates in K shell is $2 \times 1^2 = 2$, for L shell is $2 \times 2^2 = 2 \times 4 = 8$, for M shell is $2 \times 3^2 = 2 \times 9 = 18$ and for N shell is $2 \times 4^2 = 32$.

The outermost energy level of an atom cannot accommodate more than 8 electrons even if it has the capacity to accommodate more electrons. The penultimate shell (next to the outermost) cannot accommodate more than 18 electrons even if it has the capacity to accommodate more electrons.

Aufbau Principle : The electrons fill up the orbitals (sub-energy levels) in order of their increasing energies.

Mathematically, additional electron enters into that orbital for which the value of $(n + l)$ is minimum where n stands for principal quantum number and l stands for azimuthal quantum number. In case the value of $(n + l)$ is the same for two or more

orbitals, the electron will enter into that orbital for which the value of n is minimum.

The various orbitals are filled up in the following order :

$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p \ldots$

Hund's Rule of Maximum Multiplicity : It states, "No electron pairing takes place in p, d or f orbitals until all the orbitals of the given sub-level contain one electron each with parallel spins".

Pauli's exclusion Principle : According to this principle "No two electrons in an atom can have all the four quantum numbers identical". This means that no orbital can have more than two electrons and these two must have opposite spins.

Degenerate orbitals : Orbitals associated with the same energy are known as degenerate orbitals. There are three degenerate type p-orbitals (i.e. p_x, p_y & p_z), five degenerate type d- and seven degenerate type f-orbitals.

Screening Effect (Shielding Effect) : According to this "The electron clouds of inner completed sub-shells act as screen (or *shield*) for the electrons of outer orbitals against the nuclear attraction".

THE GASEOUS STATE

Perfect Gas :

Boyle's Law : At constant temperature, the product of pressure and volume of a given mass of gas is constant. The same can be expressed mathematically as

$$P \propto \frac{1}{V} \quad \text{or} \quad PV = \text{constant}$$

or $$P_1V_1 = P_2V_2$$

Charle's Law : If the pressure is kept constant, the volume of a given mass of gas is directly proportional to the temperature in absolute scale. Mathematically it can be expressed as

$$V \propto T \quad \text{or} \quad \frac{V}{T} = \text{constant}$$

or $$\frac{V_1}{T_1} = \frac{V_2}{T_2}.$$

Avagadro's Hypothesis : Under similar conditions of temperature and pressure, equal volumes of all gases contain equal number of molecules.

Ideal Gas Equation : $PV = nRT$, where n is the number of moles and R is the universal gas constant.

Molar Mass of a Gas : Let n be the number of moles of a gas, then

$$n = \frac{\text{Mass in grams of gas}}{\text{Gram molecular mass}} = \frac{m}{M}$$

also $PV = nRT$

$$= \frac{m}{M} RT \quad \text{since} \quad n = \frac{m}{M}$$

but density $(\rho) = \frac{m}{V}$ or $m = V\rho$

$$\therefore \quad PV = \frac{V\rho}{M} RT \quad \text{or} \quad P = \frac{\rho}{M} RT$$

or $M = \frac{\rho}{P} RT.$

Molar Volume of a Gas : The volume occupied by one mole of any gas at STP (standard temperature and pressure) is known as molar volume. The molar volume of a gas at STP is 22.4 litres. Also 1 mole= 6.02×10^{23} particles.

Gay-Lussac's Law : If volume remains constant, then

$$P_t = P_o (1 + at)$$

here at = absolute temperature.

or $$P_t = \frac{P_o T}{273},$$

here P = Pressure of gas at $0^{\circ}C$ and

P_t = Pressure of gas at $t^{\circ}C$

t = Temperature in $^{\circ}C$

T = Temperature in absolute scale.

Numerical value of R : $R=0.082$ atm. dm^3 $mole^{-1}$ K^{-1}, if P is measured in atmospheres and volume is measured in dm^3.

$R=8.314$ J $mol^{-1}K^{-1}$ if P is measured in pascal and v in m^3.

R represents the work of expansion of one mole of gas for one degree increase in temperature.

Graham's Law of Diffusion : Under similar conditions of temperature and pressure, the rates of diffusion of gases are inversely proportional to the square roots of their densities.

Mathematically, the same can be expressed as

$$\frac{r_1}{r_2} = \sqrt{\frac{d_1}{d_2}} = \sqrt{\frac{M_1}{M_2}}$$

Dalton's Law of Partial Pressures : When a number of gases are present in the form of a mixture, then the pressure of the mix-

ture is equal to the sum of the individual pressures of the gases present i.e.

$$P = P_1 + P_2 + P_3 + \ldots$$

where P = total pressure exerted by mixture P, P_2, P_3 are partial pressures of various gases present in the mixture.

Gay-Lussac Law of Combining Volumes : Two substances which react in gaseous state always react in rational and simple volume. A rational and simple volume ratio also exists for the products of the reaction only if they are also in the gaseous state e.g.

$$\underset{1}{N_2(g)} + \underset{3}{3H_2(g)} \rightleftharpoons \underset{2}{2NH_3(g)}$$

Kinetic Equation of an Ideal Gas :

$$PV = \frac{1}{3} nmc^2$$

where n = number of molecules in a gas

m = mass of each molecule of a gas

V = volume of gas

P = pressure exerted by the gas

c = root mean square velocity of the molecules of gas.

Mean (Average) Velocity $(\bar{c})$: It is expressed as

$$\bar{c} = \frac{c_1 + c_2 + c_3 + \ldots . c_n}{n}$$

where $c_1, c_2, \ldots c_n$ represent the actual velocity of molecules of a gas

$$\text{Also } \bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

Root Mean Square Velocity (R.M.S.). It is expressed as

$$c = \frac{\sqrt{c_1^2 + c_2^2 + \ldots c_n^2}}{n}$$

$$= \frac{\sqrt{3RT}}{M}$$

Most Probable Velocity : Velocity possessed by the largest number of molecules

is called most probable velocity and is denoted by $c_{m.p.}$

$$c_{m.p.} = \frac{\sqrt{2RT}}{M}$$

THE SOLID STATE

Solids : Solids have a definite shape and definite volume. They possess regular arrangement of constituent particles (atoms, ions or molecules).

Main Characteristics of Solids : Solids possess one or more of the undermentioned characteristics. Solids (i) are rigid (ii) have definite volume (iii) change to liquid on heating (iv) have high densities (v) are incompressible (vi) have good thermal and electrical conductivity (vii) possess definite shape (viii) are crystalline or amorphous in structure.

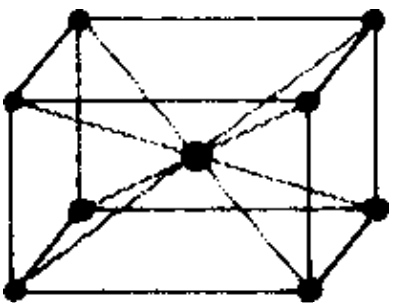
Crystal Structure : This refers to the regular and repetitive arrangement of atoms or molecules in crystals.

Space Lattice (Crystal Lattice) : The three dimensional pattern present in crystalline substance is known as crystal or space lattice. It is a network of lines drawn in space such that the space is divided into equal volumes and the points of intersection of these lines are the lattice points upon which the atoms, ions or molecules make up the substance.

Unit Cell : Unit cell is the smallest unit of lattice which when translated along the axes of the lattice produces the crystal lattice.

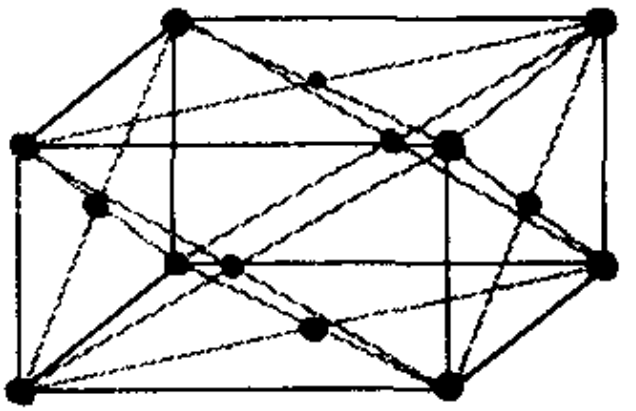
Different types of Unit Cells : Three types of unit cells are described below :

(i) Body centred cubic structure (B.C.C.)



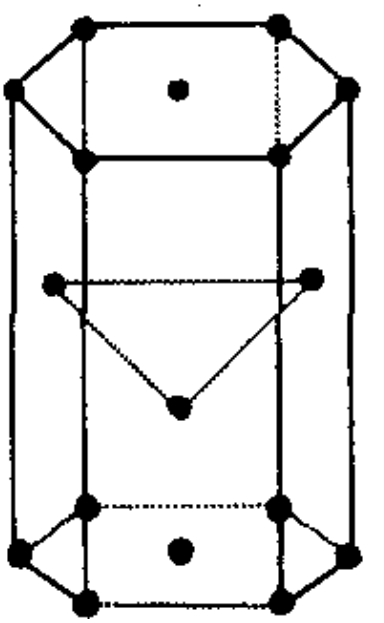
(B.C.C.)

(ii) Face centred cubic structure (F.C.C.)



(F.C.C.)

(iii) Hexagonal closed packed structure (H.C.P.) :



Primitive Cell : A crystalline cell having lattice points at the corners only, is called a primitive cell. It contains equivalent of one complete atom or molecule.

Coordination Number : It is the number of nearest atoms which are directly surrounding a given atom in a crystal.

Coordination number in (i) Case of simple cubic structure is 6.

(ii) Case of body centred cubic structure, it is 8

(iii) Case of face centred cubic structure, it is 12.

Atomic Radius : It is the half of distance between adjacent atoms in a crystal of a pure element.

Calculations of Atomic Radius : If the structure of crystal and lattice parameters are known, the atomic radius can be calculated as follows :

In simple cubic cell $r = a/2$ *where* a is the edge of the cube and r is atomic radius.

In BCC (Body Centred Cubic).

$$r = \frac{\sqrt{3}\,a}{4}$$

In FCC

$$r = \frac{a}{2\sqrt{2}}$$

Number of atoms per unit cell

In case of BBC = 2

In case of FCC = 4

In case of HCP = 6

Relative Density of Packing or Atomic Packing Factor (A.P.F.) : It is the ratio of total volume of atoms per unit cell to the total volume occupied by the unit cell

$$\text{A.P.F.} = \frac{v}{V}$$

A.P.F. in case of simple cubic structure =0.52388

A.P.F. in B.B.C. = 0.68

A.P.F. in F.C.C. = 0.74

Interstitial Sites : It can be easily seen that even in close packing of spheres, certain hollows are left vacant. These holes in the crystals are called interstitial sites. Two important sites are : (i) tetrahedral (ii) octahedral

Radius of Tetrahedral void (hole), $r = 0.225\ R$

where R = Radius of sphere in close packing
Radius of octahedral void (r) = 0.414 R.

Thus, we see that tetrahedral void is much smaller than an octahedral void. Relation between the density (ρ) and edge length of a unit cell of cubic crystal lattice

(i) Density of unit cell

$$= \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

(ii) Mass of unit cell

= Rank of unit cell×

mass of each particle = $Z \times m$

Mass of each particle =

$$\frac{\text{Molar mass of the particle}}{\text{Avogadro's number}}$$

(iii) Volume of unit cell =

a^3 where a is the edge length

(iv) For atoms : $m = \frac{M}{N_o}$

Radius Ratio : This is defined as 'the ratio of cation radius to that of the anion'.

Mathematically it is represented by

$$\frac{r^+}{r^-}.$$

Relation between Radius Ratio and Coordination Number :

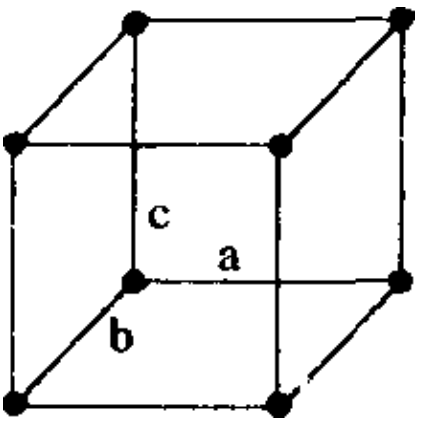
(i) When radius ratio is greater than 0.225 but less than 0.414 a coordination number of 4 is usually observed.

(ii) When radius ratio is in the range of 0.414 – 0.732, coordination number of 6 is generally observed.

(iii) When radius ratio is greater than (>) 0.732, a coordination number of 8 is usually observed.

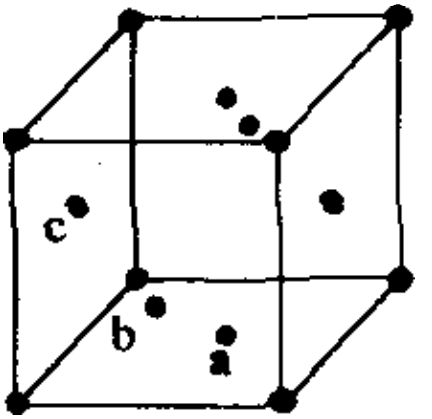
Bravais Lattices : Bravais, in 1880, proposed that there are fourteen types of space lattices in the system of crystals. A brief description of all these is given below one by one :

(i) **Simple Cubic Lattice** : It has lattice point at the eight corners of the unit cell. In this vectors

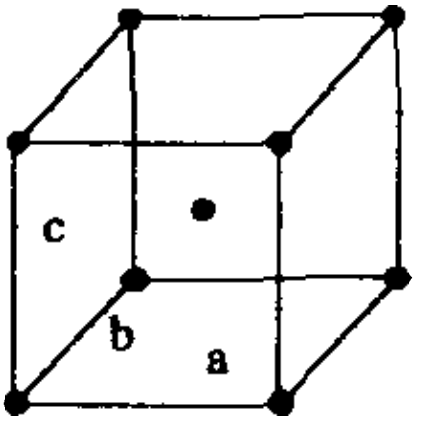


$a = b = c$ and interaxial angle $\alpha = \beta = \gamma = 90^{\circ}$.

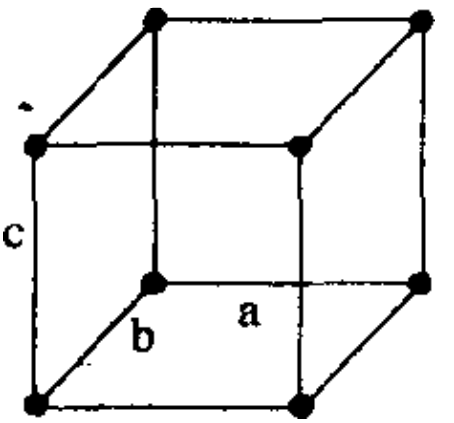
(ii) **Body Centred Cubic Lattice** : It possesses lattice points at the eight corners of a cube and one of them at the body centre. In it vectors $a = b = c$ and interaxial angles $\alpha = \beta = \gamma = 90^{\circ}$



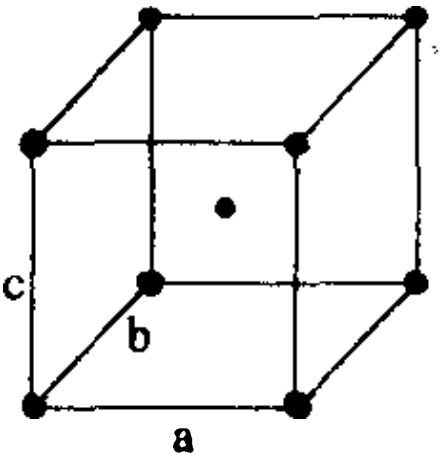
(iii) **Face Centred Cubic Lattice** : It possesses lattice points at the eight corners of a cube and an atom at the face centre of the unit cell. In it vectors $a = b = c$ and interaxial angles $\alpha = \beta = \gamma = 90^{\circ}$.



(iv) **Simple Tetragonal Lattice** : It possesses lattice point at the eight corners of the unit cell. In this vectors $a = b \neq c$ and interaxial angles $\alpha = \beta = \gamma = 90^{\circ}$.

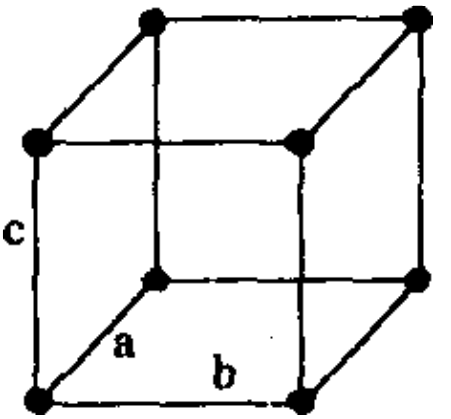


(v) **Body Centred Tetragonal Lattice** : It has lattice points at the eight corners and at the body centre. In it vectors $a = b \neq c$ and interaxial angles $\alpha = \beta = \gamma = 90^{\circ}$.

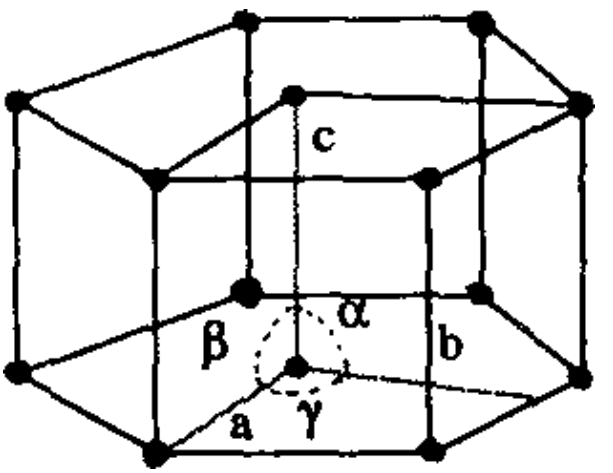


(vi) **Simple Lattice** : It has lattice points at the eight corners of the unit cell. In this vectors $a = b \neq c$ and interaxial angles $\alpha = \beta = \gamma = 90^{\circ}$.

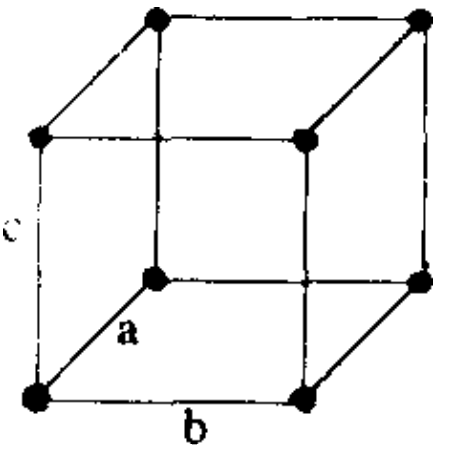
Rhomobohedral



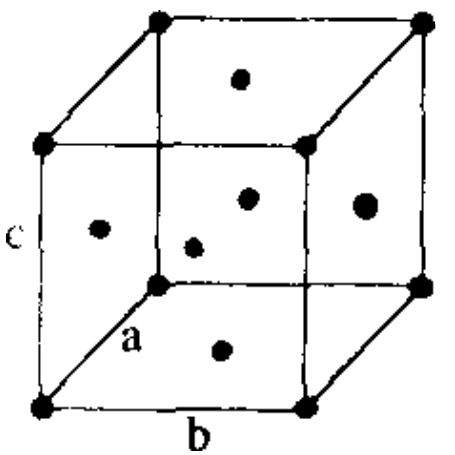
(vii) **Simple Hexagonal Lattice** : It possesses lattice points at the twelve corners of the hexagonal faces. In this vectors $a = b = c$ and interaxial angles $\alpha = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$.



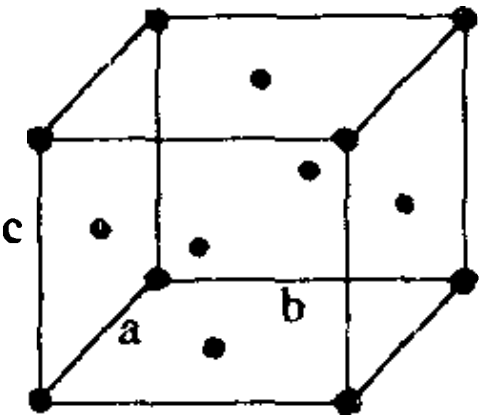
(viii) **Simple Orthorhombic Lattice** : It has lattice points at the eight corners of the unit cell. In this vectors $a \neq b \neq c$ and interaxial angles $\alpha = \beta = \gamma = 90^{\circ}$



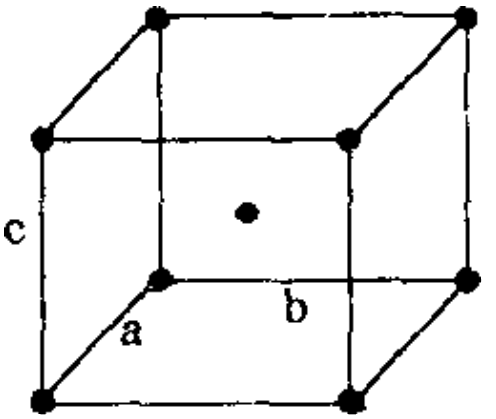
(ix) **End centred Orthorhombic Lattice** : It has lattice points at the eight corners and at the two face centres opposite to each other. This lattice is also called side centred or base centred orthorhombic lattice. In this vectors $a \neq b \neq c$ and interaxial angles $\alpha = \beta = \gamma = 90^{\circ}$.



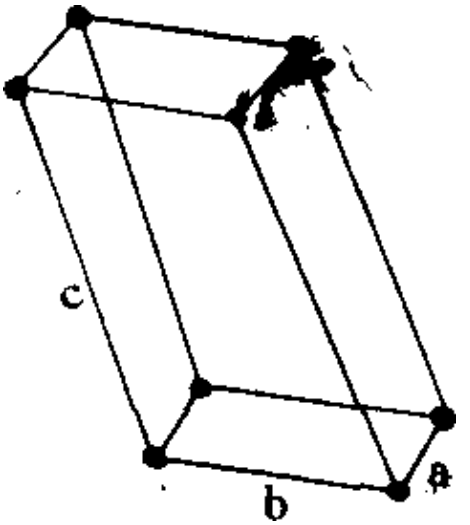
(x) **Body Centred Orthorhombic Lattice** : It possesses lattice points at the eight corners and at the body centre. In this vectors $a \neq b \neq c$ and interaxial angles $\alpha = \beta = \gamma = 90^{o}$.



(xi) **Face Centred Orthorhombic Lattice** : It has lattice points at the eight corners and at the six centres of the unit cell. In this vectors $a \neq b \neq c$ and interaxial angles $\alpha = \beta = \gamma = 90^{o}$.

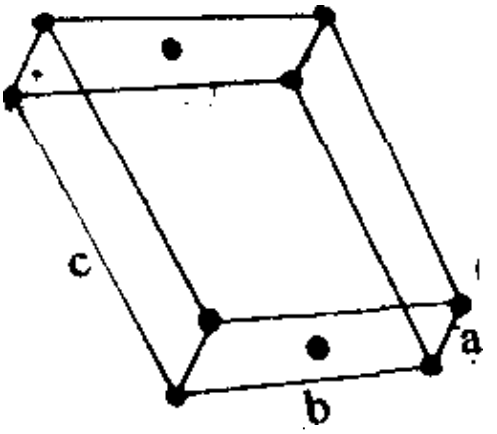


(xii) **Simple Monoclinic Lattice** : It has lattice points at the eight corners of the



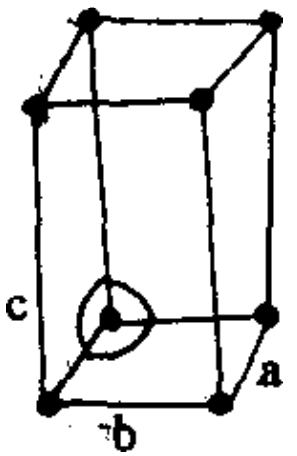
unit cell. It has vectors $a \neq b \neq c$ and interaxial angles $\alpha = \beta = \gamma = 90^{o}$.

(xiii) **End Centred Monoclinic Lattice** : It has lattice points at the eight corners



and at two face centres opposite to each other. In this vectors $a \neq b \neq c$ and interaxial angles $\alpha = \beta = 90^{o} \neq \gamma$.

(xiv) **Simple Triclinic Lattice** : It possesses lattice points at the eight corners of the unit cell. In this vectors $a \neq b \neq c$ and interaxial angles $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$.



Imperfections in Crystals : Usually majority of the real crystals are not perfect and have many imperfections. These can broadly be classified as :

(a) **Point Defects** : This includes (i) Vacancies (ii) Interstitialities (iii) Substitutional defects (iv) Schottky defects.

(b) **Line Defects** : This includes (i) Edge dislocations (ii) Screw dislocations.

(c) **Surface Defects** : These are also known as planar or interfacial defects. They

include (i) Grain boundaries (ii) Tilt boundaries (iii) Twin boundaries (Twinning).

Vacancy Defect : This defect arises when an atom is missing from a lattice site. An anion vacancy causes an excess of positive charge and so an electron can migrate to this site replacing the absent atom. This defect is known F-centre.

Interstitial Impurity : This arises when a foreign atom occupies an interstitial site.

Substitutional Impurity : This arises when a foreign atom occupied a lattice site.

Schottky defect : This defect arises in ionic solids when vacancy at cation site is accompanied by a vacancy at a nearby anion site. This defect makes an over all decrease in the density of the crystal.

Dislocation : This is used to denote line intersections which extend along some direction in crystal lattice.

F-centres : They refer to the electrons trapped in anion vacancies in a crystal lattice.

Frenkel defect : This defect arises when a cation leaves its lattice site and enters an interstitial site. This defect causes no change in the density of the crystal.

Photo voltaic : It is a solid which is used for converting sunlight into electricity e.g. amorphous silica.

Antiferro electric : A crystal is known to be anti-ferro electric if the dipoles in its alternate polyheads point up and down so that there is no net dipole moment. e.g. $PbZrO_3$ (Lead Zirconate).

Ferromagnetic Substances : They show permanent magnetism even on removal of electric field. Once these substances are magnetised they retain their magnetism permanently.

Paramagnetic substances : Such substances possess permanent magnetic dipoles due to the presence of ions, atoms or

molecules having unpaired electrons. They lose their magnetism in presence of a magnetic field.

Diamagnetic substances : Such materials do not have unpaired electrons (have only paired electrons) and are repelled by magnetic field.

Classification of Solids : Solids have been classified into following categories on the basis of bonds :

(a) **Ionic Solids** : Those which contain ionic bonds e.g. LiCl.

(b) **Molecular Solids** : They have dipole-dipole type of intermolecular forces. Sometimes such solids may have hydrogen bonding and Vander Waals forces e.g. CO_2, O_2 etc.

(c) **Metallic Solids** : Those having metallic bonds e.g. Na, Ag, Au, Cu etc.

(d) **Covalent Solids** : They have covalent bonds e.g. quartz, diamond, Silicates etc.

SOLUTIONS

Solution is a homogeneous mixture of two or more substances whose composition can be changed e.g. solution of common salt in water.

Solvent : It is the substance in which solute is dissolved. In solution it is always present in large amounts e.g. water, ammonia etc.

Solute : The substance which is dissolved in a solvent is known as solute. In solution it is present in smaller amounts e.g. sugar in a sugar solution in water.

Kinds of Solution :

(i) Gas in gas (ii) Gas in liquid
(iii) Gas in solid (iv) Solid in liquid
(v) Solid in gas (vi) Solid in solid
(vii) Liquid in gas (viii) Liquid in liquid.

Solubility : The extent to which a solid substance can be made to dissolve in a certain definite amount of solvent is known its solubility. It is expressed as the amount of

solute in grams that can be dissolved in 100 gm of the solvent at any given temperature and pressure. Different methods of expressing compositions of solutions :

(i) **Molarity** : It gives the number of moles of the solute dissolved in one litre of solution. It is expressed by M.

$$\text{Molarity, } M = \frac{n_B}{v}$$

$$= \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}}$$

(ii) **Molality** : It is the number of moles of the solute dissolved in 1000 gm of the solvent. It is denoted by m.

$$\text{Molality, } m = \frac{n_B}{W_A} \times 1000$$

$$= \frac{\text{Number of moles of solute}}{\text{Weight of solvent in grams}} \times 1000$$

(iii) **Normality** : It is the number of gram equivalents of the solute dissolved in one litre of solution. It is denoted by N.

Normality,

$$N = \frac{\text{Number of gram equivalents of solute}}{\text{Volume in litres of the solution}}$$

(iv) **Mass Percentage** : It is the number of parts by mass of a solute per 100 parts by mass of solution e.g. 15% sugar solution in water.

(v) **Mole Fraction** : It is the ratio of number of moles of one component to the total number of moles present in the solution.

Mole fraction of solute (X_B)

$$= \frac{\text{Moles of solute}}{\text{Moles of solute + Moles of solvent}}$$

$$= \frac{n_B}{n_A + n_B}$$

Mole fraction of solvent (X_A)

$$= \frac{\text{Moles of solvent}}{\text{Moles of solute + Moles of solvent}}$$

$$= \frac{n_A}{n_B + n_A}$$

Also $X_A + X_B = 1$

Mass Fraction : It is the ratio of mass of solute to the total mass of the solution.

Mass Fraction of solute

$$= \frac{\text{Mass of solute}}{\text{Mass of solute + Mass of solvent}}$$

Mass Fraction of Solvent

$$= \frac{\text{Mass of solvent}}{\text{Mass of solute + Mass of solvent}}$$

Vapour Pressure of Liquid : It is the pressure exerted by the vapour with the liquid of the same substance at equilibrium.

Lowering of Vapour Pressure : If P^o is the vapour pressure of the pure liquid and P_s is the vapour pressure of solution, then $(P^o - P_s)$ is known as the lowering of vapour pressure.

Relative Lowering of Vapour Pressure : It is the ratio of lowering of vapour pressure to the vapour pressure of pure solvent.

Relative lowering of vapour pressure

$$= \frac{(P^o - P_s)}{P^o}.$$

Boiling Point : The temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure is known as the boiling point of the liquid.

Colligative Properties : These are the properties which depend only on the number of particles of solute present into the solution and are independent of the nature of the solute e.g.

(a) Elevation of boiling point

(b) Depression of freezing point

(c) Osmotic pressure

(d) Relative lowering of vapour pressure.

The observed value of a colligative property is normal when the solute exists in solution in its normal state. It will be higher if the solute molecules undergo dissociation and lower than the normal value if the solute molecules undergo association in solution.

Roult's Law (For Miscible Liquids) : This states, "In a solution of two miscible and volatile liquids A and B, the partial pressure p_A of liquid A is proportional to its mole fraction X_A". Similarly $p_B \propto X_B$.

Mathematically,

$$p_A \propto X_A$$

or $$p_A = p_A^0 . X_A$$

Similarly, $p_B = p_B^0 . X_B$, where p_A^0 and p_B^0 are the vapour pressures of pure components A and B respectively.

Roult's Law can also be stated, "For solution of volatile liquids, the partial pressures of any component is equal to the

product of the vapour pressure of pure component and the mole fraction of that component in solutions."

Roult's Law (*for solution of non-volatile* solute) : The relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute when the solvent alone *is volatile*.

Since $p_A = p_A^0 . X_A$

or $p_A = p_A^0 (1 - X_B)$

because $X_A + X_B = 1$

or $\frac{p_A}{p_A^0} = 1 - X_B$

or $X_B = 1 - \frac{p_A}{p_A^0} = \frac{p_A^0 - p_A}{p_A^0}$

or Mole fraction of B = Relative lowering of vapour pressure for dilute solution,

$$\frac{p_A^0 - p_A}{p_A^0} = \frac{n}{N}$$

Solution which obeys Roult's Law for all concentrations is called **Ideal Solution.**

For ideal solution $\Delta V = 0$, $\Delta H = 0$

For such solution $p = p_A + p_B + \ldots$.

Examples : (a) Mixture of benzene and toluene. (b) A solution of chlorobenzene and bromobenzene. (c) Mixture of ethyl bromide and ethyl iodide.

A **non-ideal solution** is one which does not obey Roult's law. The deviation from Roult's law may be positive or negative. For such solutions $\Delta V \neq 0$, $\Delta H \neq 0$.

Examples :

Positive deviation : Ethonol-cyclohexane

Negative deviation : Chloroform-acetone.

Azeropic Mixtures or Constant Boiling, Mixtures : Such mixtures contain miscible liquids in definite proportions which boil at constant temperature and distil off unchanged in composition e.g. A mixture of 95.6% alcohol + 4.4% water (Boiling point = 78.17°C).

Components of an azeotropic mixture cannot be completely separated by distillation.

Elevation of boiling point (Ebulliscopy)

The rise in the boiling point of a solution produced by a non-volatile substance dissolved in a solvent. For a dilute solution the elevation is proportional to the number of molecules or ions present, and the elevation produced by the same molecular (ionic) concentration is a constant for a given solvent.

Elevation in b.p., $\Delta T_b = K_b . C$ or $T_b \propto m$ or $\Delta T_b = K_b . m$ where

K_b = Ebulliscopic constant of solvent

C = Molar concentration

M = Molarity of solution.

Ebulliscopic constant of some liquids :

Water = $0.52^{o}C$

Aceton = $1.72^{o}C$

Benzene = $2.47^{o}C$

Chloroform = $3.88^{o}C$

Ether = $2.11^{o}C$

Ethyl alcohol = $1.15^{o}C$

K_b (molal elevation constant) is the elevation in boiling point for 1 molal solution.

The molal elevation constant is also called ebulliscopic constant.

Relationship between Elevation in Boiling Point and Molecular Mass of Solute.

$$M_B = \frac{W_B \times K_b \times 1000}{\Delta T_b \times W_A}$$

where,

M_B = Molecular mass of solute

W_B = Weight (in grams) of solute

K_b = Molal elevation constant

ΔT_b = Elevation in boiling point

W_a = Weight (in grams) of solvent.

Depression of Freezing Point :

The freezing point of a solution is always lower than that of the solvent. This is known as depression in freezing point. Depression in freezing point;

$$\Delta T_f = K_f . m \quad \text{or} \quad \Delta T_f = K_f . c.$$

where ΔT_f = lowering of freezing point

K_f = cryoscopic constant

c = molar concentration.

Depression in freezing point of a molal solution is known as molal cryoscopic constant.

Cryoscopic constants of some liquids :

Water	1.86°C
Acetic acid	3.9°C
Benzene	5.1°C
Camphor	40.0°C
Naphthalene	6.9°C

Relationship between Depression in Freezing Point and Molecular Mass of Solute

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$

where, K_f = molal depression constant or cryoscopic constant

W_B = Weight (in grams) of solute

ΔT_f = Depression in freezing point

W_A = Weight (in grams) of solvent

M_B = Molar mass of solute.

Osmosis : Osmosis is the flow of pure solvent into a solution through a semi-permeable membrane.

Semi-permeable Membrane : This is a special type of membrane that allows the passage of solvent molecules into the solution and prevents the solute molecules or ions from passing through it, when it is placed in between a solution and solvent of different concentrations.

Osmotic Pressure : It is the hydrostatic pressure at equilibrium on the solution due to the osmosis of pure solvent. Osmotic pressure is the excess pressure that must be applied to a solution to prevent the passage of solvent into it through the semi-permeable membrane.

The osmotic pressure obeys the ideal gas type equation.

$$\pi V = nRT$$

where, V = Volume of solution

π = Osmotic pressure

n = Number of moles of solute

T = Absolute temperature

R = Gas Constant (Solution constant)

Boyle's Isothermal Law :

$$\frac{\pi}{c} \cdot t = \text{constant}$$

where, c = concentration of solution

Charles Isobaric Law :

$$\frac{1}{C_t} = \frac{1}{C_o}(1 + \alpha t)$$

where C_t = Concentration at given temp t^0C

C_o = Concentration at 0^0C

$\alpha = \frac{1}{273}$, t = temperature in ^0C

Gay Lussac's Isochoric Law :

$$\pi t = \pi_o(1 + \alpha t)$$

where, πt = osmotic pressure at t^0C

π_0 = osmotic pressure at 0^oC.

General Solution Equation :

$$\pi = C \cdot R \cdot T$$

where C = concentration – moles dm^{-1}

R = Gas constant = 0.082 atm. dm^{-1} mol^{-1} K^{-1}

T = Absolute temperature.

Relation between Osmotic Pressure and Molar Mass of Solute :

$$\pi V = n_B RT \text{ (Vant Hoff Formula)}$$

where,

π = Osmotic pressure

V = Volume of solution

n_B = Number of moles of solute

or $$\pi = \frac{W_B RT}{M_B V}$$

or $M_B = \frac{W_B RT}{\pi . V}$.

Vant Hoff Factor (i) :

i = normal molecular mass/observed molecular mass.

Diffusion : It is the phenomenon of intermixing of two or more kinds of molecules.

CHEMICAL KINETICS

Chemical Kinetics is that branch of chemistry which deals with the speed or rate of reaction.

Homogeneous Reactions : When all the reactants and products are in the same physical state, the reaction is said to be homogeneous reaction e.g.,

$$NaOH\ (aq) + HCl\ (aq) \rightarrow NaCl\ (aq) + H_2O$$

Heterogeneous Reactions : Reactions, where reactants and products are in different physical states, are known as heterogeneous reactions e.g.

$$2HCl\,(aq) + CaCO_3\,(s) \rightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O$$

Exothermic Reactions : Reactions which are accompanied by evolution (release) of heat energy are known as exothermic reactions i.e. ΔH is negative or heat of products is less than heat of reactants.

e.g., $O_2\,(g) + H_2\,(g) \longrightarrow H_2O\,(g)$;

$\Delta H = -242.7$ kJ / mole.

Endothermic Reactions : These are the reactions which are accompanied by absorption of heat energy i.e. ΔH is positive or heat of products is greater than heat of reactants e.g.,

$$C\,(s) + H_2O\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g);$$

$\Delta H = +131.8$ kJ/mole.

Different Kinds of Chemical Reactions :

(a) Chemical combination

$$H_2 + Cl_2 \longrightarrow 2HCl$$

(b) Chemical decomposition

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

(c) Simple displacement reaction

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

(d) Double displacement reaction

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

Rate of Reaction : It is defined as the decrease in concentration of the reactants or increase in the concentration of products per unit time. There occurs an increase in rate of reaction if the concentration of reactants is increased.

For a reaction $A \rightarrow B$,

$$\text{Rate of reaction} = -\frac{\Delta A}{\Delta t} = +\frac{\Delta B}{\Delta t}$$

Reaction rate constant (K) or Specific reaction rate : For a reaction, it is defined as "the rate of reaction when the concentrations of the reactants are unity". The value

of K depends upon (i) order of reaction (ii) temperature.

Average Rate :

$$\text{Average rate} = \frac{\text{Change in conc.}}{\text{Time involved for change}} = \frac{\Delta A}{\Delta t}$$

Instantaneous rate : It is the rate of the reaction determined at a particular moment of time. The average rate approaches the instantaneous rate as Δt becomes smaller.

Factors which affect the rate of reaction :

(a) Physical state of reactants — rate of reaction increases with increase in surface area.

(b) Concentration of reactants – rate of reaction increases with increase in concentration.

(c) Catalyst – it generally increases in presence of catalyst.

(d) Temperature – rate of reaction increases with increase in temperature.

Rate Equation : It is a mathematical expression that shows the relationship between the rate of the reaction and the concentration of reactants.

$$A + B \longrightarrow C + D$$

$$\text{Rate} = -\frac{d(A)}{dt} = -\frac{d(B)}{dt} = +\frac{d(C)}{dt} = +\frac{d(D)}{dt}$$

This equation is called rate equation.

Order of a Reaction : It is equal to the total number of reacting species (ions, atoms or molecules) whose concentration actually changes during the course of a chemical reaction.

For a general reaction

$$A + B + C \longrightarrow \text{Products}$$

If, rate $= K[A]^p . [B]^q . [C]^r$ [rate equation]

where K is rate constant, then order of the reaction = $(p + q + r)$.

Molecularity of Reaction : It is equal to the sum of coefficients of various reactants appearing in a balanced chemical equation

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 2C_6H_{12}O_6$$

For the above reaction, molecularity = 1+1 = 2.

Molecularity is a theoretical concept and its value is always a whole number. If molecularity is one, it is unimolecular. If molecularity is two, it is bimolecular and so on.

First Order Reaction : In case the rate of reaction is found to be directly proportional to the concentration (first power of concentration) of a single reactant, it is said to be first order reaction

$$A \rightarrow \text{Products}$$

$\frac{d(A)}{dt}$ = rate = $K[A]$ [rate equation for first order]

Examples of First order reaction :

(i) Rate of growth of bacterial culture.

(ii) Rate of growth of population, if there is no change in birth rate and death rate.

(iii) Radioactive disintegration process.

Rate Constant for a First Order Reaction.

$$A \rightarrow B$$

If 'a' is the initial concentration of A and 'X' of it disappears in time 't'. Then concentration of A after time 't' is $(a - x)$, therefore

$$K = \frac{2.303}{t} \log \frac{a}{a - x}$$

Units of K = sec^{-1}.

Second order Reaction : This is a reaction whose rate is directly proportional to the square of concentration of a single reactant or equal to the concentration of two different reactants.

For such a reaction

$$A + B \longrightarrow \text{Products}$$

$$\text{rate} = K[A][B] \text{ or rate} = K[A]^2$$

$$k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)},$$

where a, b *are the initial concentrations of* A and B respectively and $(a - x)$, $(b - x)$ are the concentrations of A and B after time 't'. Units of k = L $m^{-1}sec^{-1}$.

Third order Reaction : This is that reaction whose rate is found to be directly proportional to the cube of the concentration of a single reactant or equal to the square of concentration of one reactant and concentration of another reactant.

$$\text{rate} = K\,[A]^3$$

$$\text{rate} = K\,[A]^2[B]$$

$$\text{rate} = K\,[A]\,[B]^2$$

$$\text{rate} = K\,[A]\,[B]\,[C]$$

Units of $K = L^2 mol^{-2} sec^{-1}$.

Zero order Reaction : For such a reaction

$$\text{rate} = K\,(\text{concentration})^0$$

Units of $K = L\ mol\ L^{-1} sec^{-1}$.

Half-Life of a Reaction : It is the time taken for a reaction to reach the half of its initial concentration. It is denoted by $t_{1/2}$.

For a first order reaction $t_{1/2} = \frac{0.693}{K}$, *where K is the first order reaction constant.*

Reaction Mechanism

Collision Theory : Molecules react when they collide in a preferential direction.

Threshold Energy : It is the minimum amount of energy from zero level, the react-

ing molecules must possess, in order to react. It is denoted by E_T.

Activation Energy : It is defined as, "the extra energy over and above the average potential energy of the reactants which must be supplied to the reactants to enable them to cross over the energy barrier between the reactants and products." It is denoted by E_a.

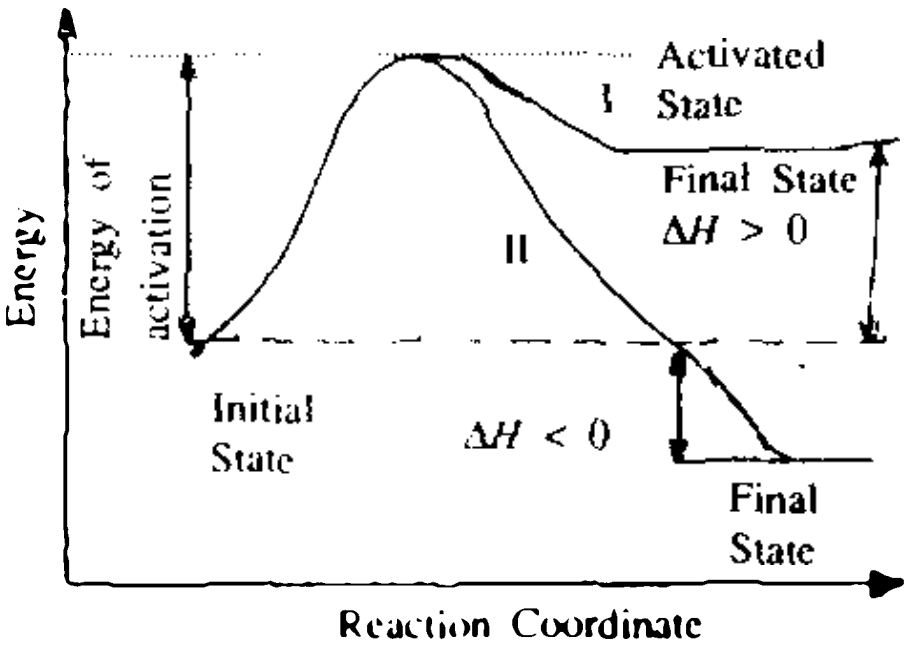
Activation energy (Ea) = Threshold energy (E_T) – Average energy of reactants (E_R)

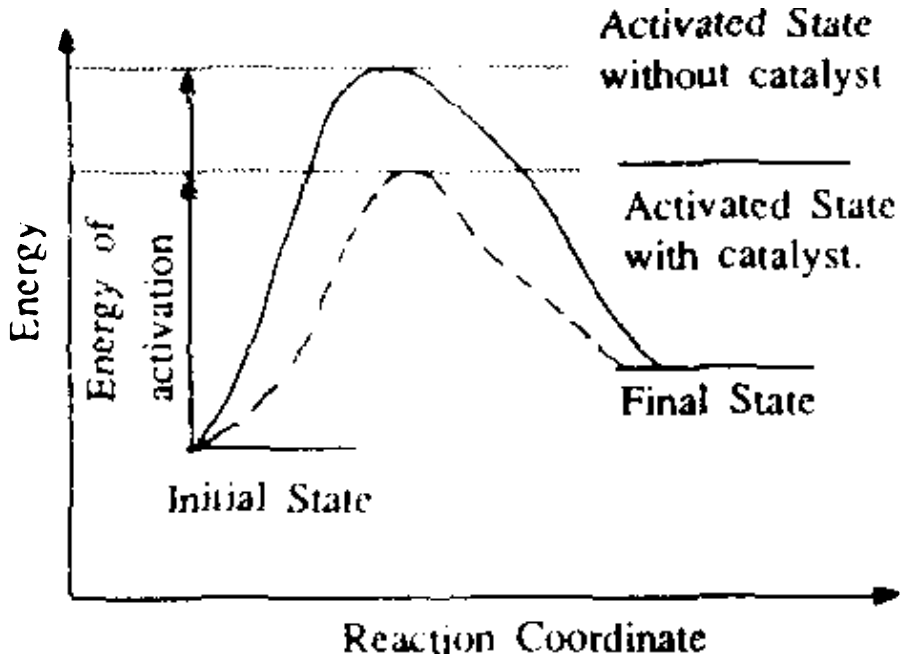
i.e. $E_a \approx E_T - E_R$

For fast reactions activation energies are low. For slow reactions activation energies are high.

Theory of Transition State : Chemical reactions occur through an intermediate stage which is known as transition state or activated state.

Particles in collision react only if, upon impact, they attain the energy of the transition state.


Energy
Energy of activation
Activated State
I
Final State
$\Delta H > 0$
II
Initial State
$\Delta H < 0$
Final State
Reaction Coordinate


Energy
Energy of activation
Activated State without catalyst
Activated State with catalyst.
Final State
Initial State
Reaction Coordinate

$\Delta H > 0$ endothermic reaction (curve I)

$\Delta H < 0$ exothermic reaction (curve II)

The catalyst reduces the energy of the transition state hence it increases the rate of reaction.

Catalyst's Effect on Equilibrium Constant : A catalyst does not alter the equilibrium constant of a reaction.

Effect of Catalyst on Activation Energy : A catalyst lowers the activation energy.

Effect of Catalyst on Free Energy Change : A catalyst does not alter the free energy change of the reaction.

Photochemical Reaction : It is the reaction which is brought about by light. The process of photography is based on light, when silver bromide is exposed to light it is decomposed

$$2AgBr\,(s) \longrightarrow 2Ag\,(s) + Br_2\,(g)$$

Example : (a) Photosynthesis by plants, (b) Bleaching action of sun.

Photosensitisation : Some substances react upon the exposure of light only in presence of a particular substance which is known as photosensitisation. It helps to start the photochemical reaction. Its function is to carry energy e.g. in the photosynthesis of plants, chlorophyll (green pigment in plant leaves) acts as photosensitizer.

ELECTROCHEMISTRY

Electrochemistry is the branch of chemistry which is concerned with the study of relationship between electrical energy and chemical energy and conversion of one form into another.

Electrochemical Reactions : Reactions involving the flow of current are called electrochemical reactions. The following are different types of electrochemical reactions.

(i) **Electrolysis :** These reactions require electrical energy from external source to bring about a chemical change. (Electrical energy is consumed)

(ii) **Electrochemical Cells :** In these cells the electrical energy is produced due to the chemical changes taking place inside the cell.

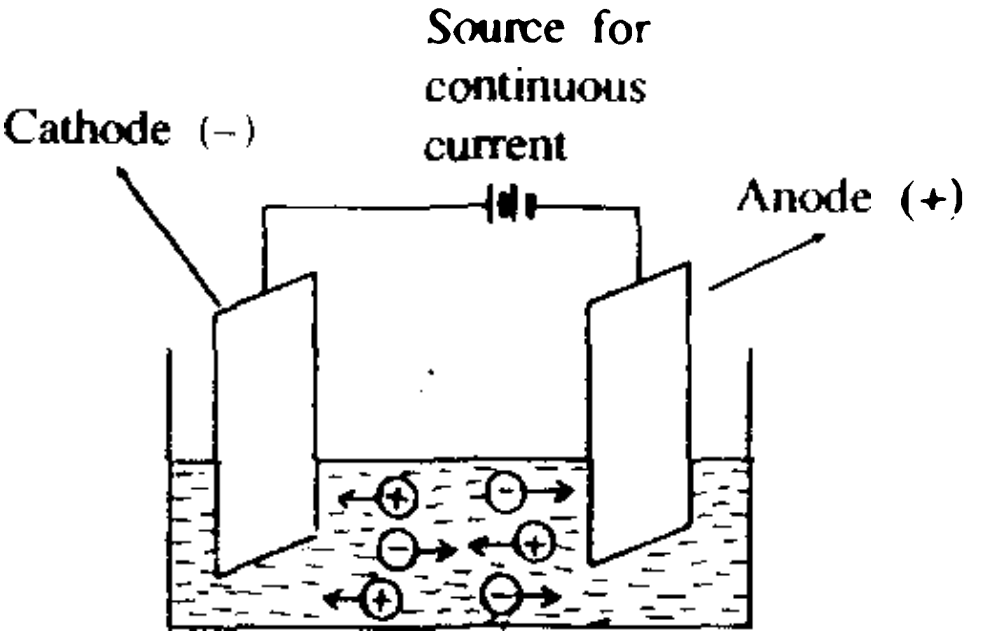
Electrolytes : Substances which conduct electricity in the molten state, fused state or aqueous solutions are known as electrolytes.

Conductors : Those substances which allow the passage of current through them are called conductors.

Metallic Conductors : Those metallic substances which allow the passage of electricity through them without undergoing any chemical change are called metallic conductors e.g. silver, copper, aluminium etc.

Metallic Conductance : It is the phenomenon of flow of electrons through a metallic substance. It occurs due to flow of electrons.

ELECTROLYSIS



(i) Process :

(A) Migration of ions to electrodes of opposite sign.

(B) Anode oxidation and simultaneous cathode reduction

Anode (+) : $A^- \rightarrow A + e^-$

Cathode (–) : $M^+ + e^- \rightarrow M$

when A^- is anion and M^+ is a cation.

(ii) Basic Equation for Electrolysis :

$$E_{app} = E_{cell} + E_{ov} + iR$$

where E_{app} is potential applied to the electrodes.

E_{ccll} is potential of the cell when current is not flowing;

E_{ov} is over potential at the electrodes;

i is current;

R is total resistance of the cell circuit.

(iii) Constant Current Electrolysis : Electrolysis is carried out by continuously regulating E_{app} so as to keep the current constant and measuring the time needed for electrolysis to be completed. The process is expressed by Faraday's law

$$M = \frac{(M.M)\, i \,.\, t}{nF}, \text{ where}$$

M = Mass in grams of the ion given off at the electrode.

M.M = Molecular mass of ion.

i = Current in amperes.

t = time in seconds.

n = number of moles of electrons involved in reaction.

F = Faraday constant (96500 coulombs).

Electrolytic Conduction : The phenomenon of flow of current through an electrolytic solution is called electrolytic conduction.

Non-Electrolytes : Substances which do not conduct electricity either in their molten state or through their aqueous solutions.

Weak Eletrolytes : Substances which are poor conductors in solution are known as weak electrolytes e.g. organic acids, organic bases, water etc. Such substances are poorly ionised in solution.

Strong Electrolytes : Substances which give high conductivities in solutions are called strong electrolytes. Such electrolytes

are almost completely ionised in solution e.g. mineral acids, salts, alkalies etc.

Conductivity : *When voltage (V) is applied across a metallic conductor or an electrolyte, it offers resistance (R) to the flow of current.*

Ohm's Law : It states, "Potential difference across the conductor is directly proportional to the current flowing through it".

Mathematically, $V \propto I$

or $$\frac{V}{I} = R \text{ (constant)}$$

or $$V = IR$$

V is the potential difference, I is the strength of current and R is the resistance of conductor.

Resistance (R) of any conductor is the obstruction offered to the flow of current.

Mathematically, $R \propto l$, where l is the length.

or $R \propto \frac{l}{a}$ (a is the area of cross section)

or $R = \rho \frac{l}{a}$ where ρ is the proportionate constant and is known as specific resistance.

$$\rho = \frac{R \cdot a}{l}$$ unit of R – ohms

Specific Resistance : It is the resistance offered by the conductor of 1 cm length and having one sq cm as area of cross-section. This is the resistance offered by a centimeter cube of a conductor. Its unit is ohm-cm.

Conductance (C) : It is reciprocal of resistance (R) which is expressed as :

$$C = \frac{1}{R}$$

Its unit is ohm^{-1} or mho.

Electrical conductance is also expressed in seimens (S). It is a measure of the ease

with which a current flows through a conductor.

Specific Conductance (K) : Reciprocal of specific resistance is known as specific conductance. It is also defined as the conductance of one centimeter cube of the conductor.

$$K = \frac{1}{\rho} = \frac{1}{R}\left[\frac{1}{a}\right]$$

Its unit is $ohm^{-1}cm^{-1}$ or seimen cm^{-1}.

Equivalent Conductivity of Electrolytic Solution : It is expressed by the equation

$$\lambda m \text{ (Equivalent conductivity)} = \frac{K}{C_{eq}}$$

where, C_{eq} is the concentration of solution in equivalents per litre.

K is conductivity (specific) of solution. It may also be defined as the conducting power of all the ions produced by dissolving 1gm-equivalent of electrolyte in solution

$$\lambda_{eq} = \frac{K \times 1000}{C_{eq}}$$

here, C_{eq} is the normality of solution. Units are $ohm^{-1}cm^2equi^{-1}$ or S, cm^2 $equi^{-1}$.

Molar Conductivity: It is the conducting power of all the ions produced by dissolving one gram mole of an electrolyte in solution. It is represented by Δm and mathematically expressed as

$$\Delta m = \frac{K \times 1000}{M}$$

where, K is specific conductance and M is molarity of solution.

Variation of Molar Conductivity with Concentration

It is expressed as

$$\Delta m = \Delta_m^{\alpha} - b\sqrt{c}$$

where, Δm is molar conductivity at given dilution. Δ_m^{α} is molar conductivity at infinite

dilution b is constant and C is concentration of solution.

As $C \longrightarrow 0, \quad \Delta_m \approx \Delta_m^{\alpha}$

Effect of Dilution on Molar Conductivity : It increases with increase in dilution.

Degree of Dissociation : Degree of dissociation is the fraction of electrolyte that dissociates into ions. For weak electrolytes it is expressed as

$$\alpha = \frac{\Delta_m^c}{\Delta_m^{\alpha}}$$

where Δ_m^c is molar conductance at concentration c.

Kohlrausch's Law : This law states, "at infinite dilution when the dissociation of an electrolyte is considered complete, each ion makes a definite contribution towards the molar conductivity of electrolyte irrespective of association with other ions".

Thus, $\Delta_m^\alpha = \nu_+ . \Lambda_+^\alpha + \nu_- . \Delta_-^\alpha$

where and ν_+ and ν_- are the numbers of cations and anions respectively. Δ_+^α and Δ_-^α are molar conductivities of cations and anions respectively.

For example

$$\Delta_m^\alpha (KCl) = \Delta_{K^+}^\alpha + \Delta_{Cl^-}^\alpha$$

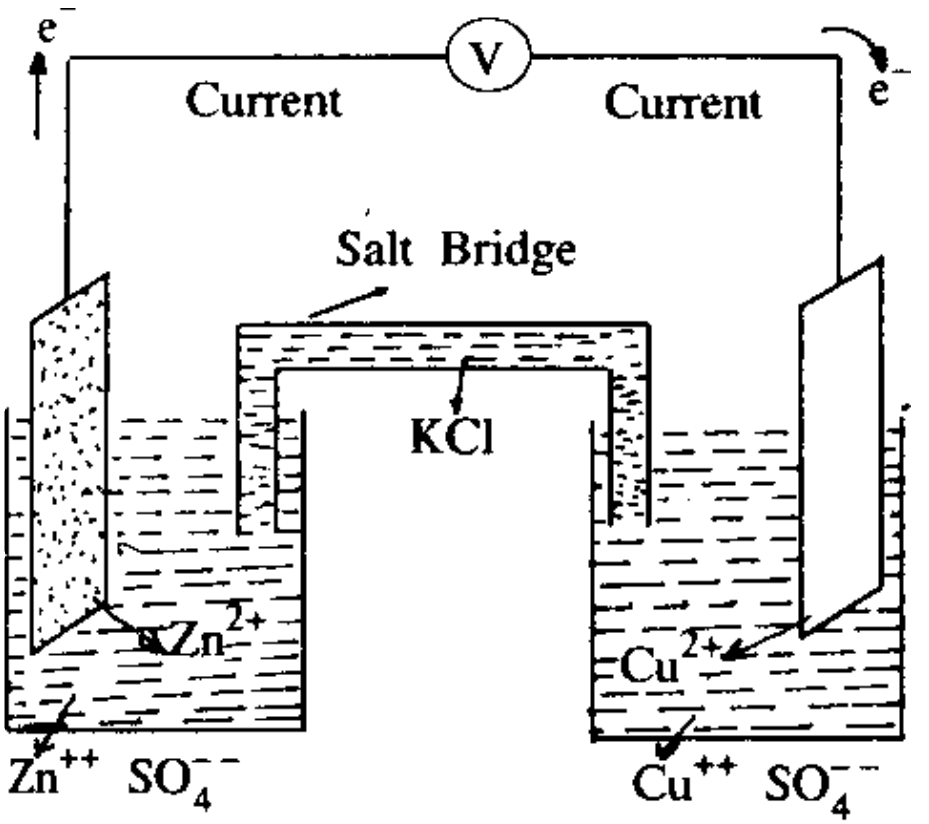
Every ion has a definite value of Δ_m at infinity.

Voltaic or Galvanic cell : This cell is a simple device of producing electrical energy by chemical reactions. Such a cell is also known as an electro-chemical cell.

$Zn \rightarrow Zn^{2+} + 2e$ (oxidation) at Anode

$Cu^{2+} + 2e^- \rightarrow Cu$ (Reduction) at Cathode

In the Galvanic cell, zinc electrode is anode and the copper electrode is cathode.



Galvanic Cell

Electrolytic Cell : It is a device to convert electrical energy into chemical energy.

Electrode Potential : It is the potential developed over an electrode when it is immersed into the solution of its own ions. It is denoted by E.

Oxidation Potential : It is the tendency of an electrode to lose electrons in a half cell.

Reduction Potential : It is the tendency of an electrode to gain electrons in a half cell.

Standard Electrode Potential : It is the electrode potential of an element in contact with its own ions when the concentration of it is one molar (1 M) at 25°C. It is denoted by E^o.

Hydrogen Electrode : It is used as a reference electrode. Its potential is taken to be zero at 25°C. A hydrogen electrode consists of a platinum strip dipped in an acid solution of 1M H^+ ion concentration and over which hydrogen gas is bubbled at 1 atmospheric pressure.

Salt Bridge : It is an inverted U-tube that contains an electrolyte (e.g. KCl). It connects the solutions of two half cells.

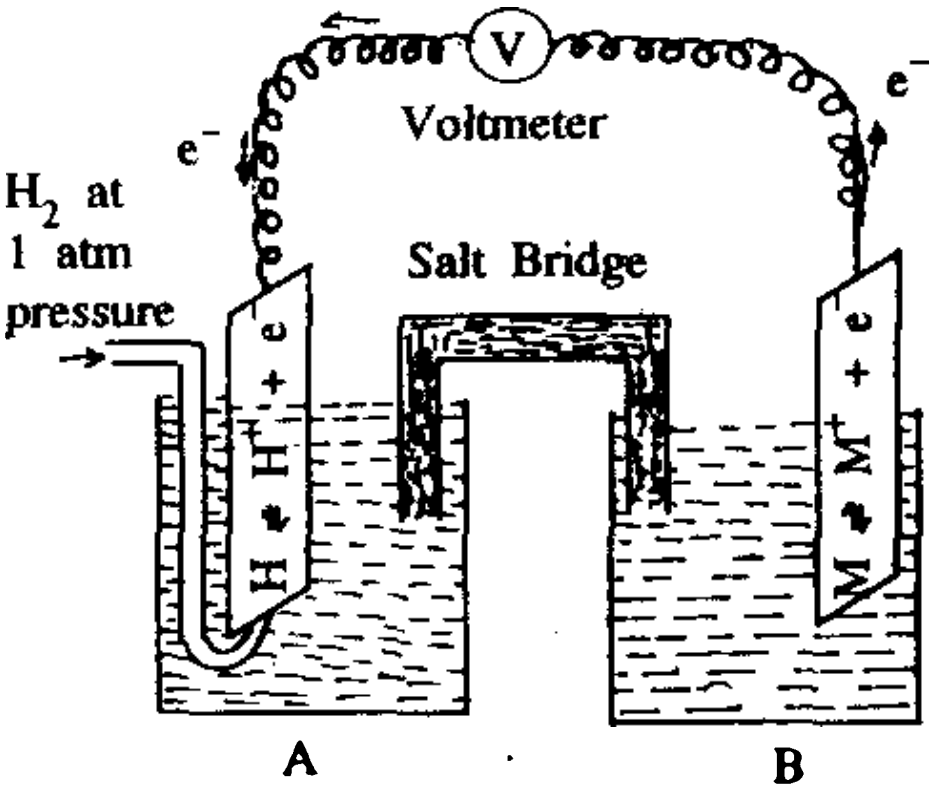
E.M.F. of the Cell : It is defined as the potential difference between the two ter-

minals of the cell when no current is drawn from it. Potentiometer is the device used to measure the potential difference of E.M.F.

Determination of Electrode Potential :

A → Acid solution of hydrogen ions of unit activity

B → Redox solution of unit activity.



Measuring of E.M.F. : It is measured with the help of potentiometer. Potentiometer is the device to measure the potential difference or E.M.F.

$$\Delta_E = E^0_{Redox} - E^0_{H_2/H^+}$$

$$E^0_{H_2/H^+} = 0 \qquad \therefore \Delta E = E^0_{Redox}$$

Potentiometry : It is an electrochemical method of analysis based on measuring the potential difference (e.m.f.) between two half-cells, one of which is an indicating electrode while the other is a reference electrode.

Indicating Electrode : It is an electrode in balance with a redox couple, the potential of which is given by Nernst's equation.

Classification of Indicating Electrodes :

(i) **First Class :** These are metallic electrodes in contact with a solution of their own ions (an electrode which is reversible in relation to the cation) M/M^{n+}.

SOME STANDARD ELECTRODE POTENTIALS		
Element	Electrode Reaction	Electrode Potential at 298°K (volts)
Lithium (Li)	$Li^+ (aq) + e^- \longrightarrow Li (s)$	-3.05
Potassium (K)	$K^+ (aq) + e^- \longrightarrow K (s)$	-2.93
Barium (Ba)	$Ba^{2+} (aq) + e^- \longrightarrow Ba (s)$	-2.90
Calcium (Ca)	$Ca^{++} (aq) + e^- \longrightarrow Ca (s)$	-2.87
Sodium (Na)	$Na^+ (aq) + e^- \longrightarrow Na (s)$	-2.71

Magnesium (Mg)	$Mg^{++}(aq) + 2e^- \longrightarrow Mg(s)$	-2.37
Aluminium (Al)	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.66
Zinc (Zn)	$Zn^{++}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76
Iron (Fe)	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.44
Nickel (Ni)	$Ni^{++}(aq) + 2e^- \longrightarrow Ni(s)$	-0.25
Lead (Pb)	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.13

Contd.

Hydrogen (H_2)	$2H^+ (aq) + e^- \longrightarrow H_2 (g)$	± 0.00
Oxygen (O_2)	$\frac{1}{2} O_2 (g) + 2H_3O^+ (aq) + 2e^- \rightarrow 3H_2O$	+1.23
Chlorine (Cl_2)	$Cl_2 (g) + 2e^- \rightarrow 2Cl^- (aq)$	+1.36
Gold (Au)	$Au^{3+} (aq) + 3e^- \rightarrow Au (s)$	+1.42
Fluorine (F_2)	$F_2 (g) + 2e^- \longrightarrow 2F^- (aq)$	+2.85

$$M^{n+} + ne^- = M$$

$$E = E^0_{M/M^{n+}} + \frac{0.059}{n} \log [M^{n+}], \text{ where}$$

$[M^{n+}]$ is concentration of cation in moles dm^{-3} and M is metal.

(ii) **Second Class :** These are metallic electrodes in contact with one of their not readily soluble salts and with the anion of this salt : $M / MA (s), A^{n-}$

$$E = E^0_{M/M^{2+}} + \frac{0.059}{n} \log K_s - \frac{0.059}{n} \log [A^{n-}],$$

where M is metal.

MA (s) is the salt which is not readily soluble $[A^{n-}]$ is concentration of the anion in moles dm^{-3} K_s is solubility product of the salt which is not readily soluble.

(iii) **Redox :** Electrodes which are inert in contact with a redox couple in solution.

Pt/ox, Red.

$$E = E^0_{Redox} + \frac{0.059}{n} \log [ox] / [Red]$$

Pt — platinum

[ox] — concentration of the oxidised form in moles dm^{-3}

[Red] — concentration of the reduced form in moles dm^{-3}

(iv) **Membrane type :** Selective electrodes specific to certain ions. They consist of a membrane which in presence of particular ions, acquires a potential which depends upon the activity of the ions in relation to those of which the electrode is selective. The best known is the glass electrode.

$$E = E_r + \frac{0.059}{n} \log a$$

E_r – constant potential linked to the choice of the reference electrode and the internal solution

a – activity of the ion in relation to which the electrode is selective.

Reference Electrode : These are the electrodes whose potential is constant and

independent of the composition of the contacting solution.

The most widely used are saturated calomel electrode (E = + 0.246 volts) and the silver chloride electrode (E = +0.222 volts).

Electrochemical Series : When standard reduction potentials of the electrodes are arranged in an increasing order, the series so obtained is called electrochemical or electromotive series.

Nernst's Equation : Nernst gave the under given fundamental electrode relation between the formal (observed) potential and the standard electrode potential for the redox reaction.

$$E_{red} = E^{0}_{red} - \frac{2.303\ RT}{nF} \log \frac{[\text{reduced form}]}{[\text{oxidised form}]'}$$

where R- Gas constant, T- absolute temperature, n-number of electrons involved in the redox reaction, E^{0} — standard reduction electrode potential, E_{Red} — observed reduc-

tion electrode potential and F is Faraday (96500 coulombs)

At 25°C, the value of the term $\frac{2.303\,RT}{F}$ comes out to be 0.0591.

So at 25°C

$$E = E^{o} - \frac{0.0591}{n} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$$

The concentration of metals is taken as unity.

Fuel Cells : They are the devices which convert chemical energy of the fuel directly into electrical energy.

Reaction in H_2–O_2 fuel cell

Anode :

$$[H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-] \times 2$$

Cathode :

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

Such a cell is used to generate electrical power in space programme.

Corrosion : It is the slow and continuous deterioration of metals and alloys by chemical or electrochemical actions of environments e.g. *rusting* of *iron*.

Chemical Corrosion involves direct chemical action between metals and gases.

Electrochemical Corrosion involves deterioration of metal due to flow of electric current from one point to another point.

***Dry* Corrosion** refers to corrosion of metals involving direct chemical action between metals and dry gases where as **wet corrosion** involves flow of electric current from one point to another through some perceptible distance in the presence of liquid or moisture of air.

Electrochemical theory of Rusting :

Reaction at anode : $Fe \longrightarrow Fe^{2+} + 2e^-$

Reaction at Cathode :

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$$

The ferrous ions (Fe^{2+}) formed at anode are oxidised by oxygen to Fe^{3+} (ferric) ions which combine with hydroxyl ions (OH^-) to yield hydrated Ferric Oxide.

$$2Fe^{2+} + H_2O + O \longrightarrow 2Fe^{3+} + OH^-$$

$$2Fe^{3+} + 6OH^- \longrightarrow 2Fe(OH)_3 \text{ or}$$

$$Fe_2O_3 . 3H_2O \text{ (Rust)}$$

Measure to prevent corrosion :

(i) use of anti-rust solutions

(ii) Barrier protection

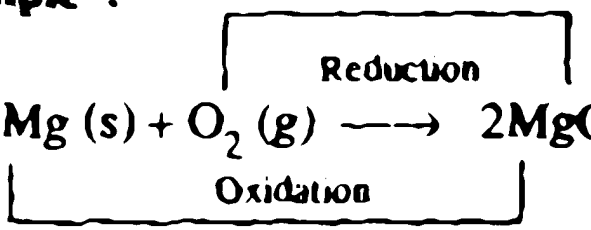
(iii) Electrical protection

(iv) Sacrificial protection.

REDOX REACTIONS

Redox Reaction : Any reaction in which transfer of electrons takes place from one reactant to another is known as a redox reaction.

Example :



A redox reaction involves both oxidation and reduction.

Oxidation : Oxidation is reaction in which an atomic or ionic system changes into a more electropositive or less electronegative state by the loss of one or more electrons.

$$Na \longrightarrow Na^{+} + e^{-}$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$$
$$2Cl^{-} \longrightarrow Cl_2 + 2e^{-}$$

Thus oxidation means increase in positive charge or decrease in negative charge.

Reduction : Reduction is a reaction in which an atomic or ionic system changes into a more electronegative or less electropositive state by the gain of one or more electrons.

$$S + 2e^- \longrightarrow S^{--}$$
$$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$$

Thus reduction means decrease in positive charge or increase in negative charge.

Oxidising Agent : It is a substance that can accept one or more electrons and is, therefore, itself reduced.

Reducing Agent : It is a substance that can furnish (donate) one or more electrons and is, therefore, itself oxidised.

Oxidation Number : It is the charge that an atom of the element appears to possess in a molecule when the electrons around it are counted according to following rules :

(i) electron pair shared between two like atoms is equally divided between the two atoms.

(ii) electron pair shared between two unlike atoms is counted with electronegative atom.

Rules to Calculate Oxidation Number (O.N.) :

(i) O.N. of an element in free state (uncombined state) is zero.

(ii) Oxygen in all its compounds has O.N. –2 except peroxides where it has O.N. –1 and oxygen difluoride (OF_2) in which it has +2 O.N.

(iii) Hydrogen in all its compounds exhibits +1 O.N. except in metal hydrides where it shows –1 O.N.

(iv) The algebraic sum of oxidation numbers of all elements in a molecule must always be equal to zero.

(v) The algebraic sum of oxidation numbers of all elements in a radical, e.g. SO_4^{--}, is equal to the charge possessed by the radical.

Oxidation - Reduction in terms of Oxidation Number :

Oxidation : It is a reaction in which oxidation number of an element increases.

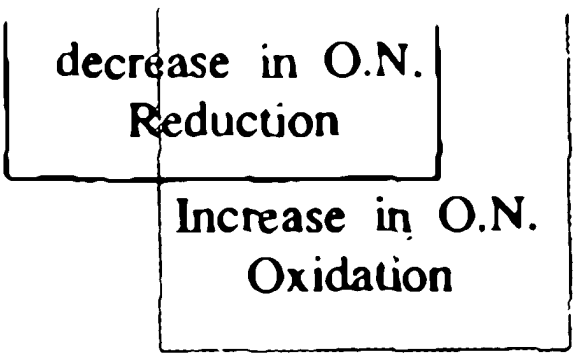
Reduction : It is a reaction in which oxidation number of an element decreases.

Oxidising agent : It is the species which undergoes a decrease in oxidation number.

Reducing agent : It is the species which undergoes an increase in oxidation number.

Example :

$$\underset{+2}{3CuO} + \underset{-3}{2NH_3} \longrightarrow \underset{0}{3Cu} + \underset{0}{N_2} + 3H_2O$$

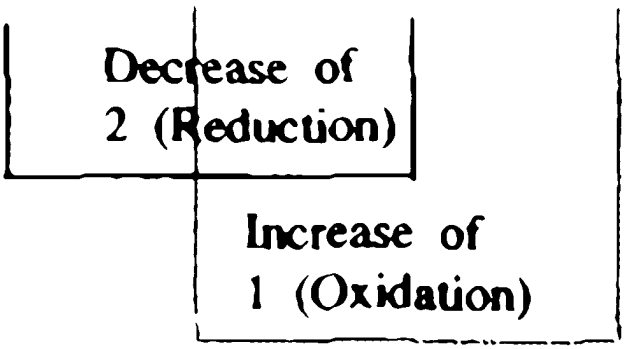


How to balance a Chemical Equation by *Oxidation Number Method* : The first step in this method is to note the elements which undergo change in oxidation numbers. The next step is to select suitable coefficients for the oxidising and reducing agents so that the total decrease in oxidation number of the

former becomes equal to the total increase in oxidation number of the latter.

Example :

$$\underset{+4}{MnO_2} + \underset{-1}{HCl} \longrightarrow \underset{+2}{MnCl_2} + \underset{0}{Cl_2} + H_2O$$



To balance total decrease to total increase in oxidation number, there should evidently be 2 molecules of HCl for 1 molecule of MnO_2 i.e.

$$MnO_2 + 2HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$$

Although the equation is now balanced from oxidation number point of view but the spectator ions (which are neither oxidised nor reduced) are to be balanced by observation using simple multiples.

Two additional chlorine atoms are required whose oxidation number remains the same as in HCl i.e. –1. There is also shortage of one oxygen atom on the right hand side. However, these atoms are to be supplied to balance the equation. Therefore, the final equation, after adjusting the coefficients of HCl and H_2O so as to provide the same number of Cl atoms and H atoms on each side, would be

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

How to balance an ionic equation by Ion Electron Method :

(i) Split the whole equation into half reactions, one for the change undergone by the reducing agent (oxidation half reaction) and the other for the change undergone by the oxidising agent (Reduction half reaction).

(ii) Balance both the half reactions not only with respect to the number and kind of atoms but also with regard to the number

of positive and negative charges. For this proceed as follows :

(a) Use simple multiples before each species so as to balance number of atoms except hydrogen and oxygen in both the half reactions.

(b) Add on equal number of H_2O molecules to the side deficient in oxygen in both the half reactions.

(c_1) In both the half reactions, add H^+ ions to the side deficient in hydrogen. (The medium of reaction must be acidic)

(c_2) Add H_2O molecules to the side deficient in hydrogen and an equal number of OH^- ions to the other side. (If the medium of reaction is basic or alkaline)

(d) Add electrons to the side deficient in electrons to balance charges in both half reactions.

(e) Multiply one or both half reactions by suitable multiples to equalise the

number of electrons in both the half reactions.

(iii) Add the two half reactions.

Example : Balance the following equation by ion electron method. The medium is acidic :

$$Cr_2O_7^- + NO_2^- \longrightarrow Cr^{3+} + NO_3^-$$

CHEMICAL EQUILIBRIUM

Reversible Reaction : Reaction in which some of the products formed react back to give the reactants is known as reversible reaction e.g.

	O.H.R.
(a)	$NO_2^- \rightarrow NO_3^-$
(b)	$NO_2^- \rightarrow NO_3^-$
(c)	$NO_2^- + H_2O \rightarrow NO_3^-$
(d)	$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+$
(e)	$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$
(f)	$3 \times [NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-]$
(g)	$3NO_2^- + 3H_2O \rightarrow 3NO_3^- + 6H^+ + 6e^-$

	R.H.R.
(a)	$Cr_2O_7^{-} \rightarrow Cr^{3+}$
(b)	$Cr_2O_7^{--} \rightarrow 2Cr^{3+}$
(c)	$Cr_2O_7^{--} \rightarrow 2Cr^{3+} + 7H_2O$
(d)	$Cr_2O_7^{--} + 14H^{+} \rightarrow 2Cr^{3+} + 7H_2O$
(e)	$Cr_2O_7^{--} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O$
(f)	$1 \times [Cr_2O_7^{--} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O]$
(g)	$Cr_2O_7^{--} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O$

Adding up the two half reactions we get

$$Cr_2O_7^{--} + 14H^{+} + 6e^{-} + 3NO_2^{-} + 3H_2O \longrightarrow 2Cr^{3+} + 7H_2O + 3NO_3^{-} + 6H^{+} + 6e^{-}$$

or $$Cr_2O_7^{--} + 8H^{+} + 3NO_2^{-} \longrightarrow 2Cr^{3+} + 3NO_3^{-} + 4H_2O$$

$$NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)$$

Irreversible Reaction : The reaction which proceeds only in one direction is known as irreversible reaction e.g.

$$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$$

State of Equilibrium : A system is said to be in the state of equilibrium if its properties like concentration, temperature, pressure etc., do not change with time. Thus state of equilibrium represents a balance between the two opposing forces.

Physical Equilibrium : The equilibrium between two physical states of the same substance is known as physical equilibrium e.g.

$$Ice\,(s) \rightleftharpoons Water\,(liq)$$

$$Water\,(liq) \rightleftharpoons Steam\,(g)$$

Chemical Equilibrium : It is a dynamic state of balance of a reversible reaction. At this state the rate of forward reaction be-

comes equal to the rate of backward reaction. The following are the two types of chemical equilibrium :

(i) **Homogeneous Equilibrium** : The chemical equilibrium of a homogeneous chemical reaction is called the homogeneous equilibrium. This takes place only in one phase e.g.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

gaseous phase

(ii) **Heterogeneous Equilibrium** : The chemical equilibrium of a heterogeneous reaction is called the heterogeneous equilibrium. It occurs in different phases e.g.

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

solid and gas phases

Laws of Chemical Equilibrium

Law of mass action : It states "The rate of a reaction is directly proportional to the product of active masses of the reactant."

For the reaction $A + B \longrightarrow$ Product

Rate of reaction α (active mass of A) (active mass of B)

For a general reaction

$$aA + bB \longrightarrow cC + dD$$

At equilibrium $r_1 = r_2$

$$r_1 = K_1[A]^a [B]^b$$

$$r_2 = K_2[C]^c [D]^d$$

Thus at equilibrium

$$K_1[A]^a[B]^b = K_2[C]^c[D]^d$$

$$\frac{K_1}{K_2} = K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where K_c is known as equilibrium constant.

Equilibrium Constant (K_c) : It is the product of the concentrations of the substances produced at equilibrium divided by the product of concentrations of the reacting substances, each concentration is raised to

the power equal to the coefficient of that substance (also known as stoichiometric coefficient) in the chemical equation.

Equilibrium constant (K_c) has a definite value for every reaction at particular temperature.

Equilibrium constant (K_c) is independent of presence of catalyst.

Equilibrium constant (K_c) indicates the extent to which a reaction proceeds.

Value of equilibrium constant, K_c, varies with temperature for any reaction.

For a reversible reaction, the value of equilibrium constant K_c for forward reaction is inverse of the value of K_c for backward reaction.

Concentration Quotient : The concentration ratio $\frac{[C]^c[D]^d}{[A]^a[B]^b}$ is known as concentration quotient. It is denoted by Q.

At equilibrium Q=K.

Gaseous Equilibrium (K_c) : Example

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

where

[ ] → concentration in moles dm^{-3}

K_c → equilibrium constant as a function of the concentration at a given temperature.

$$K_P = \frac{P^2 NH_3}{PN_2 . P^3H_2}$$

Here P → is partial pressure

K_p → is equilibrium constant as a function of the partial pressure.

Relationship between K_C and K_P:

$$K_p = K_c(R\,T)^{\Delta n}$$

where

$\Delta_n \rightarrow$ is variation in moles for a direct *reaction.*

$R \rightarrow$ is universal gas constant

$T \rightarrow$ is absolute temp.

Le-Chatalier's Principle : If an equilibrium system is subjected to a change reaction will take place in such a way as to counteract the imposed change e.g.

$$N_2 (g) + H_2 (g) \longrightarrow 2NH_3 (g);$$

$$\Delta H = 93.6 \text{ kJ}$$

Effect of Temperature : A rise in temperature shifts the reaction in the direction of heat absorption.

Effect of Pressure : In case of a gaseous phase reaction, an increase in pressure will help the reaction to proceed in the direction of diminution of the number of moles.

For reactions which proceed without any change in number of moles; change in pressure has no effect.

Effect of Concentration : Increase in concentration of reactants favours the forward reaction whereas increase in concentration of products favours the backward reaction.

Ionisation Constant :

$$K = \frac{\alpha^2 C}{1 - \alpha}$$

where, α is a fraction of dissociation of electrolyte.

C is concentration of electrolyte in moles/litre

$$C = \left[\frac{1}{v}\right]$$

K = Ionisation constant.

For weak electrolyte α is very small and so

$$K = \alpha^2 . C$$

$$= \frac{\alpha^2}{v} \quad \text{or} \quad \alpha = \sqrt{K v} = \sqrt{K / C}$$

ACIDS AND BASES

Arrhenious Theory : An acid is a substance which when dissolved in water produces H^+ ions.

Base is a substance which on dissolution in water produces OH^- ions.

Bronsted-Lowry Theory : Acid is a substance which can furnish (lose) a proton.

Base is substance which can accept a proton :

For every acid there is a base called conjugate base and for every base there is an acid known as conjugate acid.

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{HOH} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{Cl^-}$$

Conjugate acid-base pairs :

$$HCl \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} Cl^- \quad ; \quad H_2O \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} H_3O^+$$

Conjugate acid base pair may be defined to be the pair which is mutually converted into one another either by a gain or by a loss of a proton.

Lewis concept of Acids and Bases :

Acid is a substance which can accept a pair of electrons.

Base is a substance which can donate a pair of electrons.

$$\underset{\text{Acid}}{H^+} + \underset{\text{Base}}{NH_3} \rightleftharpoons NH_4^+$$

$$H^+ + OH^- \rightleftharpoons HOH$$

$$BCl_3 + NH_3 \rightleftharpoons Cl_3B \leftarrow NH_3$$

Ionic Product of Water :

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

or $H_2O \rightleftharpoons H^+ + OH^-$

$$K_C = \frac{[H_3O^+][OH^-]}{[H_2O]} \text{ or } \frac{[H^+][OH^-]}{[H_2O]}$$

$$= 1.8 \times 10^{-16}$$

$$[H_2O] = \frac{1000}{18} = 55.55 \text{ moles dm}^{-1}$$

$$K_W = K_C [H_2O] = [H^+][OH^-] = 1 \times 10^{-14}$$

$$[H^+] = [OH^-] = 1 \times 10^{-7}$$

where K_W is the ionic product of water at 25°C.

pH Value : It is defined as the logarithm of the reciprocal of the molar concentration of the hydrogen ion $[H^+]$ in the solution.

$$pH = \log \frac{1}{[H^+]} = -\log [H^+]$$

or $[H^+] = 10^{-pH}$

The acidity or basicity (alkalinity) of a solution is expressed by its pH.

pH scale : A solution becomes more and more acidic if its pH value decreases below 7. It becomes more and more basic if its pH increases above 7.

pOH values of a solution is the negative logarithm to the base 10 of OH^- ion concentration thus :

$$pOH = -\log [OH^-]$$

$$pH + pOH = 14.$$

Importance of PH :

(i) **In chemistry :** pH value helps in determining the conditions of reactions.

(ii) **In agriculture :** The pH value of soil helps in deciding the type of fertilizer to be used.

(iii) **In biological process :** pH of human blood is 6.7. Slight variation in pH of blood causes a lot of body ache.

pH of weak acid solution :

$$pH = \frac{1}{2} p K_a - \frac{1}{2} \log C$$

$$pK_a = - \log K_a$$

C is the concentration of undissociated acid.

K_a is ionisation constant of weak acid. It is given by

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+] [A^-]}{[HA]}$$

pH of a weak base solution :

$$pH = 14 - \frac{1}{2} pK_b + \frac{1}{2} \log C$$

$$pK_b = - \log K_b$$

here C is the concentration of undissociated base.

K_b dissociation constant of weak base. K_b is given by

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{[BH^+]\,[OH^-]}{[B]}$$

Ionisation Constants of Polyprotonic Acids :

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

$$Ka_1 = \frac{[H^+]\,[H_2PO_4^-]}{[H_3PO_4]}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$

$$Ka_2 = \frac{[H^+]\,[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

$$Ka_3 = \frac{[H^+]\,[PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$Ka_1 > Ka_2 > Ka_3$$

Relationship between K_a and K_b for a conjugated acid-base pair :

$$\underset{\text{acid}}{HA} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{base}}{A^-}$$

$HA \overset{-H^+}{\underset{+H^+}{\rightleftharpoons}} A^-$ is the conjugate acid-base pair.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$A^- \overset{+H^+}{\underset{-H^+}{\rightleftharpoons}} HA$ is a conjugate pair.

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

$$K_a \cdot K_b = 10^{-14}, \quad pK_a + pK_b = 14$$

Generally

$$pH = pK_a + \log \frac{[\text{base}]\ \text{conjugate}}{[\text{acid}]\ \text{conjugate}}$$

Solubility Product : The product of concentration of ions in saturated solution of an electrolyte at a given temperature is constant and is called the solubility product. In the case of AgCl,

$$\underset{\text{undissolved salt}}{AgCl\,(s)} \rightleftharpoons \underset{\text{ions in solution}}{Ag^+\,(aq) + Cl^-\,(aq)}$$

Equilibrium constant,

$$K = \frac{[Ag^+]\,[Cl^-]}{[AgCl]}$$

Because the concentration of undissolved substance is constant (say k) at a particular temperature. Therefore

$$K = \frac{[Ag^+]\,[Cl^-]}{[k]}$$

or $$Kk = [Ag^+]\,[Cl^-] = K_{s.p.}$$

where $K_{s.p.}$ is the solubility product.

Solubility and Solubility Product :

$$A_mB_n \rightleftharpoons mA^{n+} + nB^{m-}$$

$K_{s.p.} = [ms]^m [ns]^n$, where s is the solubility in moles/litre.

$$S = (m+n)\sqrt{\frac{K_{s.p.}}{n^n . m^m}}$$

m.n. is the index reaction and s is solubility in modes dm^{-3}.

Factors which influence the solubility of salts which are not readily soluble :

(i) **Temperature** : Increase in temperature enhances solubility.

(ii) **Common ion effect** : Addition of an electrolyte having an ion in common with the salt which is not readily soluble shifts the equilibrium in the direction of precipitation.

(iii) **Effect of Complexation** : The addition of a complexant of one of the ions of the salt which is not readily soluble shifts

the equilibrium in the direction of dissolution of the precipitate. Example :

$$Ag^+ + Cl^- \rightleftharpoons AgCl \text{ [white ppt.]}$$

$$AgCl + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$$

Neutralisation Reactions :

Neutralisation : An acid is neutralised by the addition of a base :

$$HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$$

$$2HCl + CaCO_3\,(s) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$$

Such reactions between acids and bases are called as neutralisation reactions.

To detect acid-base neutralisation, indicators are used. In aqueous solutions, neutralisation reactions are used analytically for titration of an acid and base.

Titre of a Solution : The concentration of the solution is known as the titre of a solution.

Titration : It is a process of determining the titre of a solution by adding a suitable titrating reagent of known titre.

The Equivalence Point : It is the particular point of equilibrium at which the equivalents of the titrating agent are equal to the equivalents of the solution to be titrated.

At equivalence point, we have

$$N_1 V_1 = N_2 V_2$$

where, N_1 is the normality (titre) of unknown solution, V_1 is the volume of unknown solution which is to be titrated.

$N_2.V_2$ are the normality and volume of the titrating solution.

In acid-base titrations, close to the equivalence point there is a rapid change in

pH which may be assessed by adding a suitable indicator.

Acidimetry or Alkalimetry (Acid-Base Titration) :

$$HA + BOH \rightleftharpoons BA + HOH$$

It is the acid-base neutralisation reaction.

To locate equivalent point a suitable indicator is used. The change in colour of the indicator chosen should be in the pH range given by

$$pH = pK_a \pm 1$$

(i) Titration between a weak acid and a strong base :

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

At the start :

$$[H^+] = [A^-]$$

$$pH = \frac{1}{2} pK_a - \frac{1}{2} \log C_a$$

C_a – is concentration of acid in moles dm^{-3}.

Before the equivalence point

$$[H^+] < [A^-]$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log \frac{C_s}{C_a},$$

here $[A^-] = C_s$ is concentration of salt and [HA] is concentration of the undissociated acid.

At the point of equivalence

$$[OH^-] = \sqrt{\frac{K_w}{K_a}} C_s \quad [H^+] = \sqrt{\frac{K_a K_w}{C_s}}$$

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C_s$$

(ii) Titration between a strong acid (HCl) and a strong base (NaOH) :

Before equivalence point

$[H^+] > [OH^-]$

$$[H^+] = \frac{(V_1 - V_2)N_b}{V_1 - V_2}$$

V_1 – Volume of acid of Normality N_a

V_2 – Volume of acid of Normality N_b

At the equivalence point,

$[H^+] = [OH^-]\ [H^+] = 10^{-7}$. pH = 7

After the equivalence point,

$[H^+] < [OH^-]$

$$[OH^-] = \frac{(V_2 - V_1)N_b}{V_1 + V_2}$$

$$[H^+] = \frac{K_w}{[OH^-]}$$

Indicator : Any substance which is used to indicate the equivalence point in an acid-

Table of some common Indicators			
Name	Colour in acidic solution	Colour in basic solution	pH range
Phenolph-thalene	colourless	red	8.0–9.8
Methyl red	red	yellow	4.4–6.2
Methyl orange	red	yellow	3.1–4.4
Thymol blue	red	yellow	1.2–2.8
Bromoth-ymol blue	yellow	blue	6.0–7.6
Aliz. yellow	yellow	red	10.1–12

base titration is known as acid-base indicator. Such a substance generally change colour according to the pH of solution.

Acid-base indicators are generally weak organic acids or bases whose ions have a different colour to that of undissociated molecules.

In general

$$\underset{\text{acid}}{HIn} + H_2O \rightleftharpoons \underset{\text{conjugate pair}}{H_3O^+ + In^-}$$

Colour of In^- is different from HIn.

$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$

Each indicator has a certain specified range of activity.

Redox Titration : Redox titrations, other than carried out by the potentiometric method, can be carried out in the same way as an ordinary acid-base titration.

The equivalence point is adjudged by adding organic substances which assume a distinctive colour in their oxidised and reduced forms. For a half cell :

$$In_{ox} + ne^- \rightleftharpoons In_{red.}$$

In_{ox} ⟶ coloured differently from In_{red}

$$E_{In} = E^o_{In} + \frac{0.059}{n} \log \frac{[In_{ox}]}{[In_{red}]}$$

Since the variation in colour can be perceived if

$$\frac{[In_{ox}]}{[In_{red}]} = 10$$

$$E_{In} = E^o_{In} \pm \frac{0.059}{n}$$

for $n = 1$, $E_{In} = E^o_{In} \pm 0.059$

E^o is standard potential.

REDOX INDICATORS			
Name	Colour Oxi-dation	Colour Reduc-tion	E^{0}_{tran} (in volts) at zero pH
Nitro-ferroine	Blue	Red violet	1.31
Ferrone	Blue	Red	1.06
4, 7 dimethyl ferroine (in HCl)	Green	Orange	0.88
Diphenyl benzidine	Violet	Colour-less	0.76

At the turning point, which is a function of the pH the potential which the solution must possess (transition potential) is that of the indicator when it is at 50% in the

oxidised form and at 50% in the reduced form.

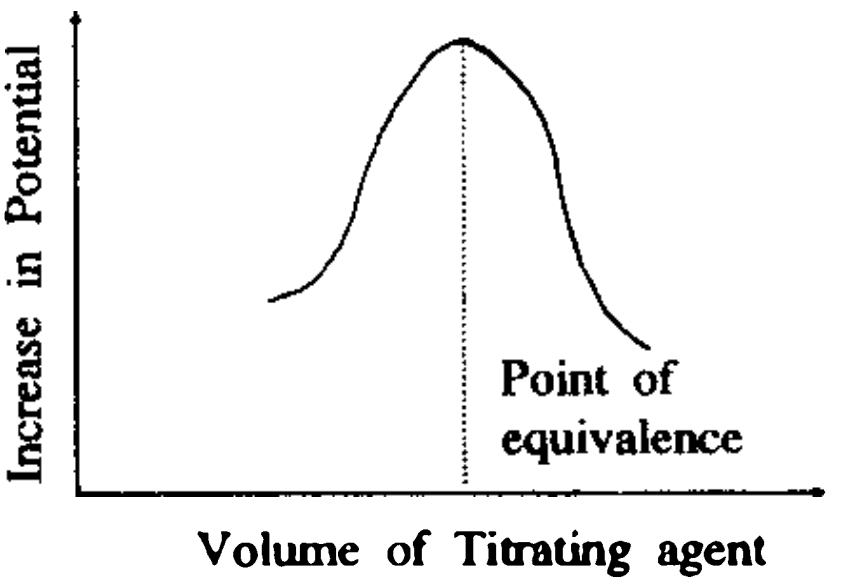
Potentiometric Titration : Titrations (acid-base, Redox, precipitation and complexation) are carried out by measuring the e.m.f. of a cell consisting of an appropriate indicating electrode, the potential of which depends on the activity of one of the ions concerned in the titration reaction and by a reference electrode connected by a saline bridge.

The graph drawn between cell e.m.f. and the volume of titrating agent shows there is a rapid variation in the e.m.f. at the point of equivalence. The form and slope of the curve depend on the stoichiometry of the titration reaction and on the equilibrium constant.

Point of Equivalence : It is the point characterised by equality of the potentials of the reductive half pair (E_2) and the oxidising half-pair (E_1).

Differential Titration : It is the curve of potentiometric titration operations carried

out by recording the increases in potential for a fixed increment of added titrating agent. It is useful in determining the point of equivalence accurately.



$$M = \frac{(M \,.\, M) \,.\, I \,.\, T}{nF}$$

Here

M → Mass in grams of the ion given off to the electrode.

M.M→ Molecular mass of the ion

I → Current in amperes

T → Time in seconds

n → number of moles of electron involved in the reaction.

F → Faraday constant (96500 couomb.)

Conductometry : It is an electrochemical method of analysis based on measuring the resistance of an electrolytic solution.

Conductivity : In an electrolytic cell having an electrolytic solution in which two electrodes are immersed and to which a potential difference (ΔV) has been applied, the following relationships exist,

$$C = \frac{1}{R} = \frac{1}{\rho} \cdot \frac{S}{L}$$

$$K = \frac{1}{\rho} = C \cdot \frac{L}{S}$$

$$C = I / \Delta V$$

where,

R stands for electrical resistance in ohms;

C stands for conductance in $ohms^{-1}$;

ρ stands for specific resistance in ohms cm^{-1};

S stands for area of the section at a right angle to the direction of current (surface of the electrodes in cm^2);

L stands for distance between two electrodes in cm;

K stands for specific conductivity in $ohm^{-1}cm^{-1}$;

I stands for current strength in amperes;

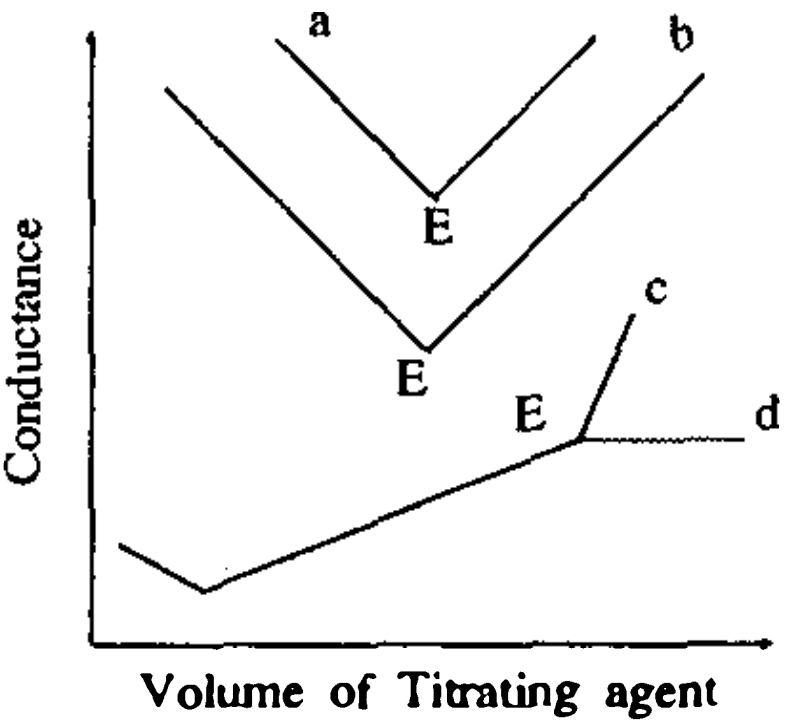
ΔV stands for potential difference applied to the electrodes in volts;

S/L = cell constant.

Conductometric Titration : The variation of conductance can be used to follow an acid-base titration and to assess the point of equivalence.

The neutralisation reaction is given as :

$$H^+ + OH^- \rightleftharpoons H_2O$$



In the graph above

a curve is for strong acid-strong base (HCl-NaOH)

b curve is for strong acid-weak base ($HCl\text{-}NH_4OH$)

c curve is for weak acid-strong base ($CH_3COOH\text{-}NaOH$)

d curve is for weak acid-weak base ($CH_3COOH\text{-}NH_4OH$)

E is *minimum* conductance-point of equivalence.

Buffer Solution : It is a solution which contains a weak acid and its conjugate base or a weak base and its conjugate acid. Buffer solution can be prepared by combining a solution of a weak acid or weak base with one of the its soluble salts e.g.

$NH_4OH\ (aq) + NH_4Cl\ (aq)$ and

$CH_3COOH\ (aq) + CH_3COONa\ (aq)$ are buffer solutions.

pH of Buffer Solution :

(i) Weak acid-base buffer.

e.g. $(CH_3COOH + CH_3COONa)$

$$pH = pKa + \log \frac{[Salt]}{[Acid]}$$

(ii) Weak base-acid buffer

e.g. $(NH_4OH + NH_4Cl)$

Some Buffer Solutions

Name	Composition of the two solutions to be mixed		pH
Ammonium buffer	NH_4OH	0.2 M	8.2 - 10.2
	NH_4Cl	0.2 M	
Delroy's buffer	Na_2CO_3(anhydrous)	0.2 M	9.2 - 10.7
	$NaHCO_3$	0.2 M	
Sorenson's buffer	KH_2PO_4	1/15 M	5.0 - 8.2
	Na_2HPO_4	1/15 M	
Welpole's buffer (Acetic buffer)	CH_3COOH	0.2 M	3.6 - 5.7
	CH_3COONa	0.2 M	

$$pH = pKa + \log \frac{[Base]}{[Salt]}$$

Hydrolysis :

Hydrolysis is the reaction between water and the ions in a salt.

(i) Salt of strong acid - strong base

Example. $Na^+ Cl^-$: The acid and the base have the same strength $\rightleftharpoons [H^+] = [OH^-]$

$$Na^+ + H_2O = Na^+OH^- + H^+$$

$$Cl^- + H_2O = H^+Cl^- + OH^-$$

pH = 7 — Neutral solution

(ii) Salt of strong acid - weak base

Example. $NH_4^+ Cl^-$

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log C$$

pH < 7 — acidic solution

(iii) Salt of weak acid–strong base

Example : $CH_3COO^-Na^+$

$$pH = \frac{1}{2} K_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

pH > 7 — basic solution

(iv) Salt of weak acid–weak base.

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

pH = 7 so $pK_a = pK_b$ (neutral)

pH > 7 so $pK_a > pK_b$ (basic)

pH < 7 so $pK_a < pK_b$ (acid)

Here,

C → Concentration of the salt in moles dm^3;

K_w → ionic product constant for water;

K_a → acid ionisation constant;

K_b → basic ionisation constant.

$pK_a = -\log K_a$

$pK_b = -\log K_b$

$pK_w = -\log K_w$

THERMODYNAMICS

Chemical Energetics : It is one of the branches of chemistry which deals with energy changes during various physical *processes and chemical reactions.*

System : Any specified part of the universe which is under investigation is known as system.

Surroundings : The rest of the universe which is not the part of the system is known as surroundings.

Types of System :

(i) **Open System** : In this system both mass and energy can be exchanged with the surroundings.

(ii) **Closed System** : In this system only energy can be exchanged with the surroundings.

(iii) **Isolated System** : It is the system in which neither mass nor energy can be exchanged with the surroundings.

(iv) **Isothermal System** : This is the system in which the reaction is carried out at constant temperature.

(v) **Adiabatic System** : In this system reaction is carried out at constant enthalpy. In this $\Delta H = 0$, temperature may vary.

(vi) **Isobaric System** : It is the system in which reaction is carried out at constant pressure.

(vii) **Isochoric System** : In this system, reaction is carried out at constant volume.

Intensive properties of a system : Properties of the system which are independent of quantity of matter contained in the system e.g. viscosity, density, refractive index etc.

Extensive properties of a system : Those properties of the system which depend upon the quantity of matter contained in the system e.g. volume, mass energy etc.

State of a system : It implies the conditions of existence of a particular system when its macroscopic properties have definite values. Any change in macroscopic properties results in a change of state of the system.

State Function : Those thermodynamic parameters which depend only upon the initial and final states of the system and are independent of the path adopted to bring about the change.

Spontaneous Reaction : Reaction which occurs of its own without any outside help is known as spontaneous reaction e.g. formation of white ppt of AgCl when $AgNO_3$ (aq) reacts with NaCl (aq).

$$AgNO_3\,(aq) + NaCl\,(aq) \rightarrow$$

$$AgCl\downarrow + NaNO_3\,(aq)$$

Internal Energy (E) : Internal energy of substance is the total sum of energies stored in it by virtue of its molecules

$$E = K.E. + P.E. + E_{trans} + E_{rot} + E_{vib} + \ldots.$$

Internal energy is a state property. The absolute value of internal energy of a system cannot be determined.

Change in internal energy (ΔE)

$$\Delta E = E_2 - E_1$$

where E_1 is internal energy in initial state and E_2 is internal energy in final state.

Enthalpy (H) : It is defined as "the internal energy plus pressure volume-work".

$$H = E + PV$$

Enthalpy is a state function. The absolute value of enthalpy of a system cannot be determined.

Change in Enthalpy (ΔH) :

$$\Delta H = H_2 - H_1$$

where H_1 is enthalpy in initial state and H_2 is enthalpy in final state.

$$\Delta H = \Delta E + P\Delta V$$

Law of Conservation of Energy : This law state "The sum total of the energy of the universe (system & surroundings) always remains constant. Although one form of energy may be converted into another form." It is also known as First law of thermodynamics.

Mathematically it is expressed as

$$\Delta E = q - W$$

where $q \rightarrow$ is heat energy change

$W \rightarrow$ is work done

$\Delta E \rightarrow$ is change in internal energy.

Hess's Law : According to this law "The enthalpy change in a chemical or physical process is same whether the process is carried out in one step or more steps".

Heat (or Enthalpy) of Formation : It is *the amount of heat evolved or absorbed* when one mole of a substance is formed from the most stable state of elements.

$$\Delta H_f = \Sigma H_{(compounds)} = \Sigma H_{(elements)}$$

Heat (Enthalpy) of Reaction : It is equal to the amount of heat evolved or absorbed as indicated by a balanced chemical equation.

Heat of Neutralisation : *It is the* amount of heat released when one gram equivalent of an acid is completely neutralised by a base.

Heat of neutralisation of a strong acid and a strong base is always 13.7 K cal/mole.

Heat of Combustion : It is the amount of heat released by complete combustion of one mole of the substance.

Heat of Fusion : It is the amount of heat required to change 1 mole of substance from solid state to liquid state.

Heat of Vapourisation : It is the amount of heat required to convert 1 mole of a substance from liquid state to gaseous state.

Heat (Enthalpy) of Sublimation : It is the enthalpy change that accompanies the conversion of one mole of solid directly into gaseous state at a temperature below its melting point.

Enthalpy of Solution : It is the enthalpy change accompanying the dissolution of one mole of substance in such a large excess of solvent that further addition of solvent does not bring about any enthalpy change.

Bond Energy : It is the average amount of energy required during breaking of one mole of bonds of that type present in a molecule of a gaseous compound. The bond energy of H-H bonds in H_2 molecule is 242.0 kJ/mole.

ΔH = Bond energy of reactants – Bond energy of products.

Calorific Value : It is the energy released in the combustion of one gram of the substance (food or fuel). Its unit is K cal/gm.

Entropy : Entropy is a measure of degree of disorder of a system. It is denoted by S.

Change in Entropy (ΔS) = $S_{final} - S_{initial}$

Units of entropy = JK^{-1} $mole^{-1}$.

Free Energy (G) : It refers to the energy available for doing some useful work. Mathematically, $G = H - TS$

Change in Free Energy (ΔG)

$$\Delta G = H - T\Delta S$$

ΔG is very useful in predicting the spontaneity of a reaction.

For spontaneity ΔG must be negative.

Gib's Helmholtz Equation

$$\Delta G = \Delta H - T\Delta S$$

Criterion for spontaneity of a reaction :

From $\Delta G = \Delta H - T\Delta S$, we get the following criterion for spontaneity.

If ΔG is negative or less than zero, the reaction is spontaneous.

If ΔG is equal to zero, the system is in equilibrium.

If ΔG is positive, the process does not occur.

Third Law of Thermodynamics : *It states* "At absolute zero, the entropy of a perfectly crystalline substance is taken to be zero."

SURFACE CHEMISTRY

Surface chemistry is the branch of chemistry which deals with the nature of surfaces and changes taking place on the surfaces.

Absorbent : It is the material on whose surface the absorption occurs.

Adsorbate : The molecular species that gets adsorbed is known as adsorbate.

Adsorption : The phenomenon of higher concentration of molecular species (liquids of gases) at the surface of a solid than in the bulk is called adsorption.

Desorption : It refers to the process of removal of an adsorbed substance from the surface on which it is adsorbed.

Chemisorption (Chemical adsorption) : If the adsorbate is held on surface by strong chemical bonding forces, the adsorption process is known as chemisorption.

Physiosorption (Physical adsorption) : If the adsorbate is held on a surface by weak Vander Waals forces, the adsorption process is known as physiosorption.

Absorption : It is a phenomenon in which the molecules of a substance are uniformly distributed throughout the body of other substance.

Positive Adsorption : When the concentration of the adsorbate is more on the surface of the adsorbent as compared to its concentration in the bulk then it is known as positive adsorption.

Negative Adsorption : If the concentration of the adsorbate is less on the surface

of the adsorbent as compared to its concentration in the bulk then it is called as negative adsorption.

Factors affecting adsorption of gas on solid :

(i) Nature of adsorbate (solid)

(ii) Nature of gas

(iii) Temperature

(iv) Activation of adsorbate

(v) Pressure

Freundlich Isotherm : It is a graph between $\log \frac{x}{m}$ and log p. It is a straight line.

Adsorption Isobar : It is a graph between the amount of substance adsorbed per gram $\left(\frac{x}{m}\right)$ and temperature 't' at constant pressure.

Applications of Adsorption :

(i) In gas masks to remove poisonous gases such as CH_4, CO etc. (activated charcoal).

(ii) For removing the hardness of water, in ion-exchange resins.

(iii) In volumetric analysis as adsorption indicator (fluorescein).

(iv) For removal of moisture and controlling humidity (silica).

(v) In decolourisation of sugar (animal charcoal).

(vi) In chromatographic purification of compounds. (silica gel.).

(vii) In creating high vacuum. (charcoal cooled in liquid air).

Colloidal State : It is an intermediate state between true solutions and suspensions. It is heterogeneous and consists of two phases.

(a) disperse phase (colloidal particles)

(b) dispersion medium (the medium in which colloidal particles are dispersed).

The size of colloidal particles ranges between 1 nm to 10 nm.

Lyophilic Colloids : Colloids in which particles of dispersed phase have a great affinity for the dispersion medium are called Lyophilic colloids e.g. glue, gelatin etc.

Lyophobic Colloids : Colloids in which there is no affinity between particles of dispersed phase and the dispersion medium are called Lyophobic colloids e.g. $Al(OH)_3$ solution.

Multimolecular Colloids : They consist of aggregates of particles of small molecules with diameter less than 1 mm e.g. solution of gold particles.

Macromolecular Colloids : They consist of dispersed particles which are large molecules e.g. polymers.

Classification of Colloids.

Dispersed Phase		Dispersion medium	Name of colloidal solution	Example
1.	Gas	Liquid	Foam	Soda water, creams, soap lather
2.	Gas	Solid	Solid Foam	Rubber, foam, bread
3.	Liquid	Gas	Aerosol	Cloud, mist, fog
4.	Liquid	Liquid	Emulsion	Milk, medicines, emulsified oils

Classification of Colloids.				
5.	Liquid	Solid	Gels	Butter, cheese, jelly
6.	Solid	Gas	Solid aerosol	Curd, smoke, boot polish, dust storm
7.	Solid	Liquid	Solu-tions	Paints, muddy water
8.	Solid	Solid	Solid solu-tions	Alloys, minerals, coloured glass, gem stones

Micelles : Colloidal solutions which behave as strong electrolytes at low concentrations but exhibit colloidal properties at higher concentration are known as Micelles. They are also known as associated colloids.

Demulsification : The decomposition of an emulsion into its constituent liquids is called demulsification.

Dialysis : This is the method used to separate impurities from the colloidal solution. It is based on the principle that colloidal particle cannot pass through a cellophane membrane or parchment while the ions of an electrolyte can pass through it.

Tyndall Effect : If a strong beam of light is allowed to pass through a colloidal solution placed in dark, the path of the beam is illuminated by a bluish light. This is because of the scattering of light and this phenomenon is known as Tyndall effect.

Electrophoresis : It refers to the movement of colloidal particles towards cathode

or anode under the influence of electric field.

Catalyst : Catalyst is a substance which increases the rate of chemical reaction without being used in the reaction.

Homogeneous Catalysis : When the catalyst mixes homogeneously with the reactants and forms a single phase, the catalyst is said to be homogeneous and the process is known as homogeneous catalysis.

Heterogeneous Catalysis : When the catalyst forms a separate phase with the reactants then it is called heterogeneous catalyst and the process is known as heterogeneous catalysis.

Activity of Catalyst : The ability of a catalyst to accelerate the rate of a chemical reaction is known as activity of catalyst. Sometimes it may be as high as 10^{10} times.

Selectivity of Catalyst : It refers to the ability of catalyst to direct reactions to yield particular products e.g. n-heptane selectively

gives toluene ($C_6H_5 - CH_3$) on platinum catalyst.

Shape Selective Catalyst : The catalytic reactions depending on the pore structure of catalysts are known as shape selective catalytic reactions and the catalysts are known as shape selective catalysts e.g. zeolite catalysts.

PART - II

Inorganic Chemistry

ELEMENTS AND COMPOUNDS

Element : Element is a substance which cannot be split up into two or more simpler substances by usual chemical methods of applying heat, light or electric energy. It is made up of atoms. Ex. Gold, Silver, Iron, Copper, Sodium, Hydrogen, Helium etc.

Elements have been divided into metals and non-metals. Metals are usually solids with the exception of mercury which is liquid. Hydrogen, phosphorus, sulphur, chlorine etc. are some non-metals. The non-metallic elements are either solids or gases except bromine which is a liquid.

Chemical Symbols : The symbol of an element is "the first letter" or "the first two letters" of the English, Greek or Latin name of an element. The symbol of hydrogen is H (first letter of name), the symbol of copper is Cu (first two letters from the Latin word cuprum). The total number of elements known at present is 105. Out of these first 92 elements (from hydrogen to uranium) occur in nature and are known as naturally occurring elements. The remaining elements after uranium do not occur in nature and have been synthesised artificially in laboratory and are, therefore, called synthetic or artificial elements.

Atomic Mass : The atomic mass of an element is the numerical number which indicates how many times an atom of an element is heavier than the mass of hydrogen atom or 1/12 mass of carbon (12) atom . For example the atomic mass of sodium is 23 which indicates that one atom of sodium is 23 times heavier than hydrogen atom or 1/12 of a carbon (12) atom. The atomic mass

unit (a.m.u.) and atomic weight unit are just the same.

Gram Atomic Mass : The atomic mass of an element expressed in grams is known as gram atomic mass. Gram atomic mass is also known as gram atomic weight.

Molecular Mass : The number of times a molecule of the compound is heavier than $\frac{1}{12}$ of the mass of carbon (12) atom is known as its molecular mass.

The molecular mass of a substance expressed in gram is known as gram molecular mass. The molecular mass is equal to the sum of the atomic masses of all the atoms present in one molecule of the substance. For example one molecule of water (H_2O) contains two atoms of hydrogen and one atom of oxygen so molecular mass of H_2O is 2H + 16=18.

Table of Elements, their Symbols and Atomic Weights

Atomic No.	Name of Element	Symbol	Atomic Weight
1	Hydrogen	H	1.0008
2	Helium	He	4.0026
3	Lithium	Li	6.9390
4	Beryllium	Be	9.0122
5	Boron	B	10.8110
6	Carbon	C	12.0115
7	Nitrogen	N	14.0067
8	Oxygen	O	15.9994
9	Fluorine	F	18.9994
10	Neon	Ne	20.1790

Atomic No.	Name of Element	Symbol	Atomic Weight
11	Sodium	Na	22.9898
12	Magnesium	Mg	24.3120
13	Aluminium	Al	26.9815
14	Silicon	Si	28.0860
15	Phosphorus	P	30.9738
16	Sulphur	S	32.06401
17	Chlorine	Cl	35.6300
18	Argon	Ar	39.9480
19	Potassium	K	39.0980
20	Calcium	Ca	40.0800

Atomic No.	Name of Element	Symbol	Atomic Weight
21	Scandium	Sc	44.956
22	Titanium	Ti	47.9000
23	Vanadium	V	50.9400
24	Chromium	Cr	51.9960
25	Manganese	Mn	54.9380
26	Iron	Fe	55.8470
27	Cobalt	Co	58.9332
28	Nickel	Ni	58.7100
29	Copper	Cu	63.5400
30	Zinc	Zn	65.3700

Atomic No.	Name of Element	Symbol	Atomic Weight
31	Gallium	Ga	69.7200
32	Germanium	Ge	72.5900
33	Arsenic	As	74.9216
34	Selenium	Se	78.9600
35	Bromine	Br	79.9040
36	Krypton	Kr	83.8000
37	Rubidium	Rb	85.4700
38	Strontium	Sr	87.6200
39	Yttrium	Y	88.9050
40	Zirconium	Zr	91.2200

Atomic No.	Name of Element	Symbol	Atomic Weight
41	Niobium	Nb	92.9060
42	Molybdenum	Mo	95.9400
43	Technetium	Tc	98.9060
44	Ruthenium	Ru	101.0700
45	Rhodium	Rh	102.9050
46	Palladium	Pd	106.4000
47	Silver	Ag	107.8700
48	Cadmium	Cd	112.4000
49	Indium	In	114.8200
50	Tin	Sn	118.6900

Atomic No.	Name of Element	Symbol	Atomic Weight
51	Antimony	Sb	121.7500
52	Tellurium	Te	127.6000
53	Iodine	I	126.9044
54	Xenon	Xe	131.3000
55	Cesium	Cs	132.9050
56	Barium	Ba	137.3400
57	Lanthanum	La	138.9100
58	Cerium	Ce	140.1200
59	Praseodymium	Pr	140.9070
60	Neodymium	Nd	144.2400

Atomic No.	Name of Element	Symbol	Atomic Weight
61	Promethium	Pm	147.0000
62	Samarium	Sm	150.0500
63	Europium	Eu	151.9600
64	Gadolinium	Gd	157.2500
65	Terbium	Tb	158.9240
66	Dysprosium	Dy	162.5000
67	Holmium	Ho	164.9300
68	Erbium	Er	167.2600
69	Thulium	Tm	168.9340
70	Ytterbium	Yb	173.0400

Atomic No.	Name of Element	Symbol	Atomic Weight
71	Lutetium	Lu	174.9700
72	Hafnium	Hf	178.4900
73	Tantalum	Ta	180.9480
74	Tungsten	W	183.8500
75	Rhenium	Re	186.2000
76	Osmium	Os	190.2000
77	Iridium	Ir	192.2000
78	Platinum	Pt	195.0900
79	Gold	Au	196.9670
80	Mercury	Hg	200.5900

Atomic No.	Name of Element	Symbol	Atomic Weight
81	Thallium	Tl	204.3700
82	Lead	Pb	207.1900
83	Bismuth	Bi	208.980
84	Polonium	Po	210.0000
85	Astatine	At	210.0000
86	Radon	Rn	222.0000
87	Francium	Fr	223.0000
88	Radium	Ra	226.0500
89	Actinium	Ac	227.0000
90	Thorium	Th	232.0380

Atomic No.	Name of Element	Symbol	Atomic Weight
91	Protactinium	Pa	231.0360
92	Uranium	U	238.0300
93	Neptunium	Np	237.0500
94	Plutonium	Pu	239.0000
95	Americium	Am	243.0000
96	Curium	Cm	245.0000
97	Berkelium	Bk	249.0000
98	Californium	Cf	249.0000
99	Einstenium	Es	255.0000
100	Fermium	Fm	255.0000

Atomic No.	Name of Element	Symbol	Atomic Weight
101	Mendelevium	Md	256.0000
102	Nobelium	No	259.0000
103	Lawrencium	Lw	260.0000
104	Kuchatovium	Ku	261.0000
105	Hahnium	Ha	262.0000

Compound : A compound is a substance made up of two or more elements chemically combined in a fixed ratio by weight. For example, water (H_2O) is compound made up of two elements hydrogen and oxygen chemically combined in a fixed ratio of 2:1.

Mixture : A mixture is a substance which is made up of two or more elements or compounds not chemically combined together in

indefinite proportions. For example, air is a mixture of different gases like hydrogen, oxygen, carbon dioxide, etc.

Chemical Equation : The way of representing a chemical reaction with the help of symbols and formulae of substances involved in it is known as chemical equation.

Reactants : The substances which combine or react are known as reactants.

Products : The new substances produced in a reaction are known as products. An arrow pointing in the right hand side is put between the reactants and the products.

$$Zn + HCl \rightarrow ZnCl_2 + H_2$$

Reactants Products

Balanced Chemical Equation : A balanced chemical equation has an equal number of atoms of different elements in the reactants and products e.g.

$$Zn + H_2SO_4 \dashrightarrow ZnSO_4 + H_2$$

The chemical equations are balanced by either of the following methods :

(i) Hit and trial method (ii) Partial equations method (iii) Oxidation number method (iv) Ion-electron method.

Mole :

1 mole = 6.023×10^{23} particles

1 mole =gram molecular mass

1 mole = 22.4 litres of a gas at S.T.P.

Standard Temperature and Pressure (S.T.P) :

Standard Temperature = 0°C or 273° K

Standard pressure=760 mm of mercury
or 1 atmosphere

1 atmosphere = 760 mm of mercury

1 atmosphere = 1.013×10^5 N / m^2

1 atmosphere = 1.013×10^5 Pa

1 atmosphere = 1.013 bar

Numerical Values of Gas Constant, R

$R = 0.0821$ litre atmosphere per degree kelvin per mole

$R = 8.314\ Nm\ K^{-1}mol^{-1}$

$R = 8.314\ JK^{-1}mol^{-1}$

$R = 8.314 \times 10^{-7} ergs\ K^{-1}\ mol^{-1}$

$R = 1.987$ calories $K^{-1}\ mol^{-1}$

Structure of Atom :

Following are the basic constituents of an atom :

Proton : It is a positively charged particle present into the nucleus of an atom. The charge of proton is 1.6×10^{-19} coulombs and the mass of proton is 1.672×10^{-24} g.

Electron : It is a negatively charged particle which revolves round the nucleus in fixed orbits. The charge of an electron is

1.6×10^{-19} coulombs and the mass of the electron is 9.1×10^{-28} g.

Neutron : It is an electrically neutral particle present into the nucleus of an atom. The mass of a neutron is 1.675×10^{-24} g.

Atomic Number : It is equal to the number of protons present into the nucleus of the atom of an element.

Atomic Number = Number of protons

= Number of electrons

Mass Number : It refers to the total number of protons and neutrons (i.e. nucleons) present in the atom of an element.

Mass Number = Number of protons + Number of neutrons

= Number of nucleons

Isotopes : Atoms of the same element having same atomic number but different atomic weights (i.e. mass numbers) are

known as isotopes. e.g. $^{35}_{17}Cl$, $^{36}_{17}Cl$ and $^{37}_{17}Cl$ are the three isotopes of chlorine.

Isobars : Atoms of different elements having same atomic weight (mass number) but different atomic numbers are known as isobars. e.g. K-40 and Ar-40.

DIFFERENT ATOMIC MODELS

Rutherford's Atomic Model :
Rutherford proposed this model in 1912. According to this model an atom consists of a positively charged central portion known as Nucleus. This nucleus is surrounded by electrons. The number of protons in the nucleus is equal to the number of electrons surrounding it. Hence an atom is electrically neutral.

All the mass of the atom is concentrated in the nucleus of the atom

The volume of nucleus is very small as compared to total volume of the atom.

The electrons and nucleus are held together by electrostatic forces of attraction.

Bohr's Model of Atom : Niels Bohr proposed this model in 1913. He simply modified the Rutherford's model to overcome its limitations retaining its important features. According to this model an atom consists of a small positively charged nucleus located at its centre. The negatively charged electrons revolve around the nucleus in certain definite circular paths known as energy levels. Each energy level is associated with a definite amount of energy. The energy levels are designated as K, L, M, N, etc. or are numbered 1, 2, 3, 4 etc., outwards from the nucleus.

The change in energy of an electron takes place only when it jumps from a lower energy level to a higher energy level (in this process there is gain of energy) or when it jumps from a higher energy level to a lower energy level (there is loss of energy). This means that as long as the electrons remain

in a given energy level, they neither gain nor lose energy and the atom remains stable.

De Broglie's Relationship : De Broglie suggested the following relationship between wavelength and momentum of a particle

$$\lambda = \frac{h}{mv} \text{ or } \frac{h}{\rho}$$

where

λ = wavelength of the particle

m = mass of the particle

v = velocity of the particle

h = Planck's constant (6.626×10^{34} JS)

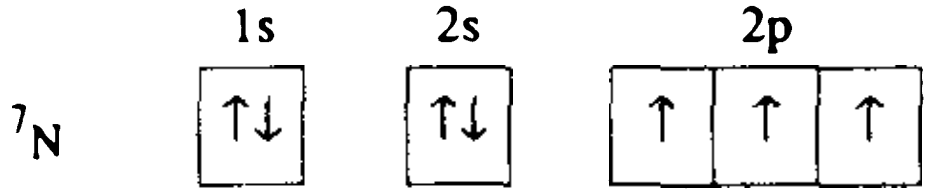
ρ = momentum of particle.

Electronic Structure of the Elements

The electrons of atoms are distributed in space over various energy levels in accordance with Pauli's exclusion principle (no two electrons in an atom can have all the four quantum numbers identical) and

Hund's rules of maximum multiplicity (for equal energy the electrons tend to have maximum distribution). e.g.

Nitrogen with At. No. 7 will have following distribution of electrons.



or $1s^2\ 2s^2\ 2p^3$

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Chemical Bonding : When a group of atoms remain together by forming a stable combination having characteristic properties, it is known as a molecule.

Ion : When an atom of molecule carries a positive or negative charge due to loss or gain of electrons, it is said to be an ion.

Cation : It is a positively charged ion that is formed when an atom loses one or more electrons. e.g. Li^{+}, Be^{++}, Cu^{+}, Au^{3+} etc.

Anion : It is a negatively charged ion which is formed when an atom gains one or more electrons. e.g. F^{-}, O^{2-}, S^{2-} etc.

Chemical Bond : Chemical bond may be defined as the attractive force that binds together the constituent atoms in a molecule. Following are some different types of chemical bonds which usually occur in various molecules.

(i) Electrovalent bond (Ionic bond) : This type of bond is formed by transfer of electrons from one atom to another. It takes place between two oppositely charged ions. In this bond, the atoms involved lose or gain electrons in order to stabilize their outer shell configuration. e.g. KCl is formed as shown below :

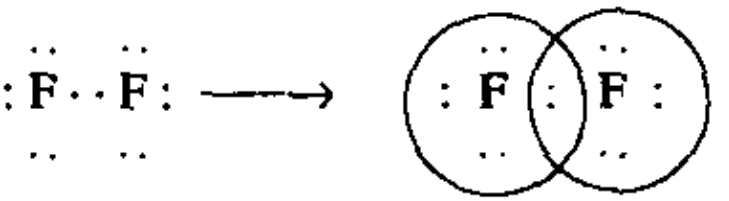
K(19) —— 2, 8, 8, 1 —— K^{+} — 2, 8, 8

Cl(17) —— 2, 8, 7 —— Cl^- — 2, 8, 8

One electron from potassium is transferred to chlorine and it results into the formation of K^+ and Cl^{-1} ions having stable configurations in their outermost shells. An electrostatic bond is formed between K^+ and Cl^- ions.

(ii) **Covalent Bond:** Such a bond arises due to the equal sharing of electrons between two atoms participating in bond formation. This bond occurs in the following three ways :

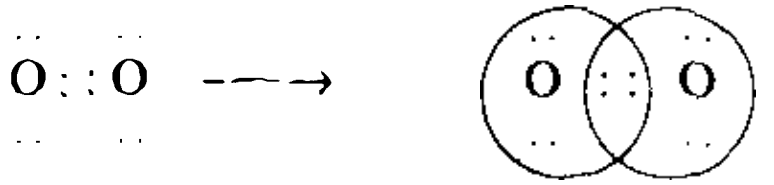
(a) Single Covalent bond : This involves the sharing of one pair of electrons between two atoms. e.g.



OR F——F

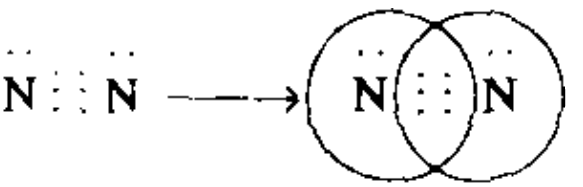
(b) Double bond : The bond between two atoms formed by sharing of two

pairs of electrons is known as a double bond. It is denoted by two horizontal lines between the two atoms. e.g.



or O = O

(c) Triple bond : It is formed by sharing of three electron pairs between two atoms and is called a triple bond. It is devoted by three horizontal lines between two atoms. e.g.



or N ≡ N

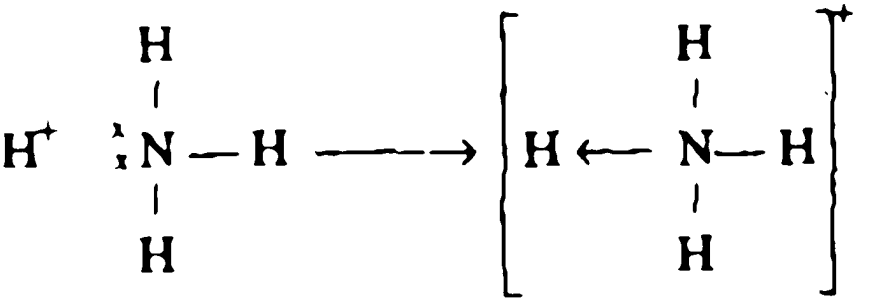
Polar and Non-Polar Covalent bond :

A polar bond is formed when the combining atoms sharing the electron pair are dissimilar. In such a covalent bond the two atoms acquire a partial positive or negative charge. The magnitude of charge depends

upon the difference of electronegativity values of the two atoms. e.g. $(H^{+\delta} - F^{-\delta})$

A non-polar bond is formed by sharing of electrons between similar atoms. e.g. H–H, F–F, Cl–Cl, etc.

(iii) Co-ordinate bond : Such a bond is formed by unequal sharing of electron pair. Here one of the participating atoms provides both the electrons (electron pair or lone pair of electrons) and it is shared by both the atoms. The atom that provides lone pair is called donor and the other atom called acceptor. This bond is denoted with an arrow pointing from donor to acceptor. e.g. NH_4^+ ion.



SOME OTHER TYPES OF BONDS

Hydrogen Bond : It is an electrostatic force of attraction acting either between the hydrogen atom of one molecule and electronegative atom of other molecule of the same substance [(intermolecular hydrogen bonding. e.g. $(HF)_n$] or between hydrogen atom and electronegative atom within the same molecule (intra molecular hydrogen bonding. e.g. O-nitrophenol)

Metallic Bond : Atoms of metallic crystals are kept together by metallic bonds. The forces in metallic bonds are of electrostatic origin. The strength of metallic bond increases with

(i) The increase in the number of electrons in the delocalised system.

(ii) The decrease in the size of the atomic core that forms the structural unit.

Vander Waals Bonding : Many atoms and molecules, though electrically neutral as a whole, contain electrostatic charge which is arranged so unsymmetrically, that they show a definite electrostatic movement.

Polarity of this type in a neutral body results from the fact that it has a positively charged region or regions. The centres of these regions are oppositely charged and exert a definite, though relatively weak attraction for each other. These weaker forces form a bond known as Vander Waals bond.

Sigma bond : This is the bond formed by the axial overlap of two orbitals belonging to different atoms. It is formed by axial overlapping of s-s, p-p, s-p orbitals.

Pi-bond : Such a bond is formed by sidewise overlapping of atomic orbitals of different atoms.

A single bond is always a $\sigma-$ bond. A double bond has a one $\sigma-$ and one $\pi-$ bond and a triple bond consists of one $\sigma-$ and two $\pi-$ bonds.

Dipole Moment : *It takes place due to* equal amount of positive and negative charge separated by a distance with in a molecule.

If dipole moment is devoted by μ, charge on the atom in coulomb by q and distance between the two charges in angstroms (A) by r then mathematically,

$$\mu = q \times r$$

Bond Energy : It is the energy needed to break a bond and to separate the bonded atoms.

Bond Length : It is the distance between the nuclei of bonded atoms. Bond length (v) of few molecules is given below :

H– Cl = 136 pm ; Cl– Cl = 198 pm

H – H = 74 pm

Electronegativity : It is the tendency of an atom to attract the shared pair of electrons towards itself in a molecule. Fluorine is the most electronegative atom.

Bond Order (B.O.) :

Mathematically, B.O. $= \frac{N_b - N_a}{2}$

where N_b = number of bonding electrons

N_a = number of anti-bonding electrons

higher the bond order more stable is the molecule. Zero bond order indicates that the molecule is not formed.

Resonance : If a molecule can be assigned two or more reasonable electronic structures and none of these is capable of explaining the known properties of the compound, then the real structure is identical exactly to none of these but an intermediate between these structures. This intermediate structure is called resonance hybrid and the phenomenon is known as resonance. e.g. the structure of carbon dioxide can be represented as

$$O = C \approx O \longleftrightarrow O =$$

$$C \dashrightarrow O \longleftrightarrow O \leftarrow C = O$$

Hybridisation : The phenomenon of intermixing of the orbitals of different energies so as to give rise to the formation of an equal number of new set of orbitals having equivalent energies and shapes. Following are the different hybridisations that occur.

(i) sp - hybridisation

(ii) sp^2 - hybridisation

(iii) sp^3 - hybridisation

(iv) dsp^2 - hybridisation

(v) sp^3d - hybridisation

(vi) sp^3d^2 - hybridisation

Valency : *It is the capacity of an element* to combine with another element which depends upon the number of electrons of the outermost orbit (valency shell) involved in the formation of a chemical bond. It is never

greater than 7. The outermost electronic configuration is responsible for the variability of the valency.

PERIODIC TABLE AND PERIODIC PROPERTIES

Prout's Hypothesis : In 1815, Prout suggested that all the elements are made up of hydrogen atoms and hence are related to each other through their atomic weights.

Law of Triads : In 1917, Dobereiner put forth his hypothesis that if elements are arranged in the groups of three in order of their increasing atomic weights having similar properties. Then the atomic weight of the middle element is the arithmetical mean of the atomic weights of the other two elements e.g.

Li	Na	K
7	23	39

$$\text{At. wt. of Na(23)} = \frac{7+39}{2} = 23.$$

Law of Octaves : Newland in 1866, gave this law according to which "when elements are arranged in order of their increasing atomic weights, the properties of eighth element (starting from a given one) are a kind of repetition of the first element like the eighth node in the octave of music."

PERIODIC TABLE

Modern Periodic Law : According to the law, "The properties of elements are the periodic function of their atomic numbers".

Periodicity : The repetition of similar chemical properties after certain interval is known as periodicity. The repetition in properties of elements is due to repetition of similar electronic configuration of outermost orbits of elements after certain intervals.

Long form of Periodic Table : It is the most commonly used form of P.T. these days. It consists of seven horizontal rows called periods and sixteen vertical columns (three columns in VIII gr) called groups.

s-block Elements : Elements of the I and II groups with outer electronic configuration ns^1 and ns^2 respectively are known as s-block elements. I group elements are called alkali metals whereas II group elements are known as alkaline earth metals.

p-block Elements : Elements in whose atoms the p-orbital of the valency shell is gradually filled up from 1 to 6 are known as p-block elements. The elements placed on the right hand side of P.T. in III and subsequent groups upto zero group are called p-block elements. The general electronic configuration of these elements is given as ns^2np^{1-6}.

d-block Elements : These elements lie in between s-block and p-block elements and consist ten vertical columns (groups). In these elements the d-sublevel of the penultimate shell is progressively filled from 1 to 10 while the s-sublevel of ultimate shell is already filled up. The general electronic configuration of d-block elements can be given

as $(n-1)d^{1-10}ns^{1-2}$. These are also known as transition elements since their properties lie in between the properties of s- & p-block elements.

f-block Elements : f-block elements have incomplete f-orbitals in the antepenultimate shell while d-orbital of penultimate shell is partially filled and s-sublevel of ultimate shell has the required number of electrons. f-block consists of two series of 14 elements each placed at the bottom of the periodic table. The first series from At. No. 58 to 71 is known as Lanthanide series whereas the second series from At. No. 89 to 103 is called actinide series.

Lanthanides (Lanthanons) : The 14 elements (from At. No. 58 to 71 i.e., from ce to Lu) immediately following lanthanum (57) in the periodic table are known as lanthanides. The properties of these elements are quite similar therefore should be placed with La (57). To avoid sidewise expansion

of the table, they have been placed at the bottom of P.T.

Actinides : The fourteen elements following actinium (89) from At. No 90 to 103 i.e., from Th to Lw in the P.T. are known as actinides. Their properties are quite similar and they have been placed at the bottom of P.T.

Noble Gases : They are the members of zero group in the P.T. The group consists of He, Ne, Ar, Kr, Xe and Rn. Except Helium which has only two electrons all other gases have eight electrons in their outermost shell.

Halogens : It is the group of p-block elements which is known as VII group. It has F, Cl, Br and I. They are non-metals and are strongly electronegative in nature which possess seven electrons in their valency shell.

Atomic Radius : It is half of the distance between the nuclei of two adjacent atoms.

Covalent Radius : It is half of the distance between the nuclei of two similar atoms held together by pure covalent single bond.

Vander Waals Radius : It is half of the distance between the nuclei of two atoms in a solid compound which are not chemically bonded. The concept is applicable to noble gases.

Variation of Atomic Size : It decreases on moving across from left to right in a period and increases on going down the group.

Ionisation Energy or Ionisation Potential (I.E. or I.P) : It is the minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom.

$$M\,(g) \xrightarrow{I.E.} M^{+} + e^{-}$$

I.E. increases on moving across from left to right in a period and it decreases on going down a group.

Electron Affinity : It is just opposite to I.E. It is defined as the amount of energy released when an extra electron is added to an isolated gaseous atom.

$$M(g) + e^- \longrightarrow M^- + E_a$$

Here E_a is electron affinity. The value of electron affinity increases going across the period and decreases on going down a group.

Electronegativity : It is the tendency of an atom to attract the shared pair of electrons towards itself in a molecule. Electronegativity increases while moving across the period from left to right in the periodic table and decreases while going downwards in a group. The electronegativity values of zero group elements i.e. inert gases are zero.

Chemical Reactivity : It is the tendency of an element to lose or gain electrons in a chemical reaction. For metals this reac-

tivity decreases from left to right in a period while it increases for non-metals.

In a group the chemical reactivity for metals increases from top to bottom and for non-metals it decreases going downwards in a group.

CHEMISTRY OF NORMAL ELEMENTS

Normal elements are the s- & p-block elements of the periodic table in which the additional electron enters into the outermost orbit (valency shell). s-block includes elements of I and II groups placed on the extreme left side of the periodic table. Elements of p-block include III and subsequent groups placed on the right side of periodic table i.e. from Boron family to inert gases

s-block Elements :

I Group Elements or Alkali Metals : Li, Na, K, Rb, Cs and Fr are the elements of I group which are known as alkali metals. Their general electronic configuration of

outermost orbit is ns^1. Following are the reactions which the alkali metals undergo :

$$2\,M + O_2 \longrightarrow M_2O_2 \quad (M \text{ is Na})$$

$$4\,M + O_2 \longrightarrow 2\,M_2O \quad (M \text{ is Na, K, Rb})$$

$$2\,M + X_2 \longrightarrow 2\,MX \quad (X \text{ is H, Cl})$$

$$2\,M + 2H_2O \longrightarrow 2\,MOH + H_2$$

II Group Elements or Alkaline Earth Metals : Be, Mg, Ca, Sr, Ba and Ra are the the elements of II group which are also known as alkaline earth metals. The general electronic configuration of the outermost orbit (valency shell) of these elements is ns^2.

Alkaline earth metals impart characteristic colours to flame.

Calcium — Brick red

Strontium — Crimson red

Barium — Green

Diagonal relationship refers to observed similarity of some elements of second period

to the diagonally situated elements belonging to next group and next period. e.g. Li with Mg, Be with Al, B with Si etc.

Uses of Alkaline Earth Metal Compounds :

(i) Beryllium is used as a window material in x-ray apparatus.

(ii) Beryllium is also used for making containers of atomic fuel.

(iii) Chlorophyll (a complex of magnesium) present as pigment in green plants helps in the process of photosynthesis.

p-block Elements :

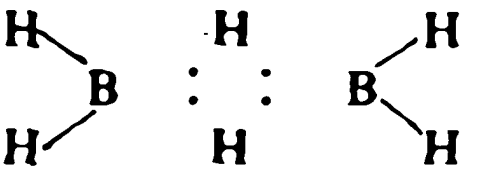
Group III Elements (Boron family) : The elements of this group are B, Al, Ga, In and Tl. The general electronic configuration of the valency shell of these elements is ns^2np^1.

Boron halides BX_3 are electron deficient molecules in which the central atom B has six electrons around it and is therefore in

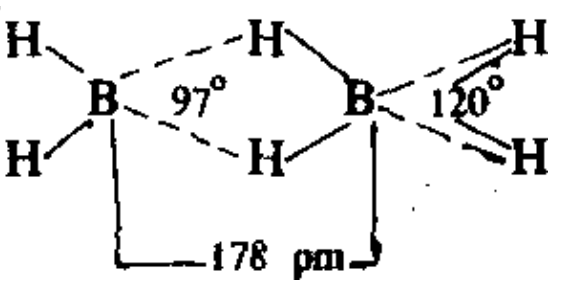
short of two electrons. These molecules thus act as strong Lewis acids.

Anhydrous aluminium chloride is also an electron deficient compound and exists as a dimer Al_2Cl_6 in an inert solvent as well as in vapour state.

Structure of Diborane (B_2H_6) :



OR

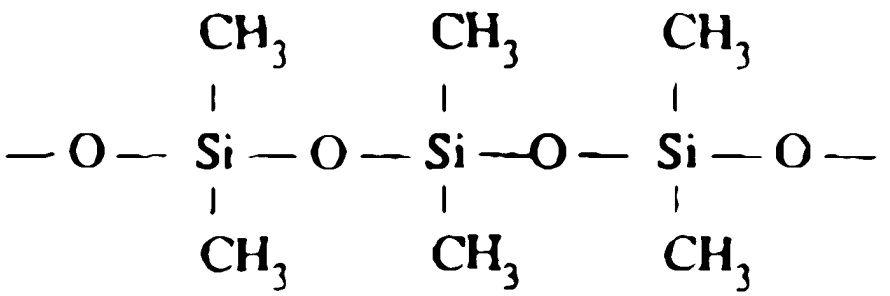


IV Group Elements (carbon family) : This group contains C, Si, Ge, Sn, Pb. Their general electronic configuration of the valency shell is ns^2np^2.

Catenation is the property of forming bonds with the atoms of the same element.

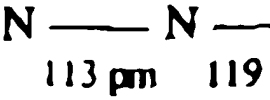
Carbon shows this property to a greater extent and forms a large variety of compounds containing carbon-carbon chains.

Silicones are synthetic polymers containing repeated R_2SiO units where R is an alkyl group. e.g.

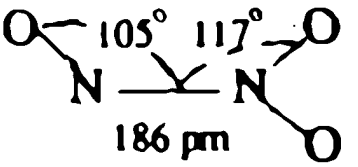


Group V Elements (Nitrogen Family) : The elements of this group are N, P, As, Sb and Bi. The general electronic configuration of the valency shell of these elements is ns^2np^3.

Structures of the Oxides of Nitrogen :

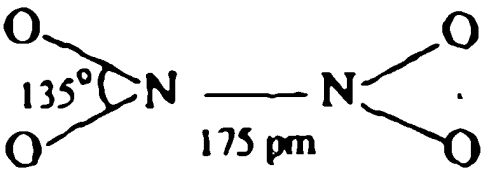
(i) N_2O  (Colourless gas)

(ii) NO N —— O
115 pm
(Colourless gas, paramagnetic)

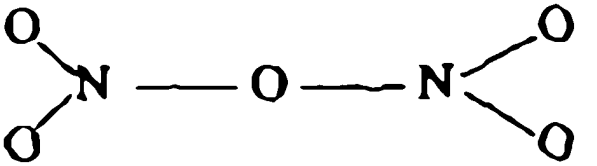
(iii) N_2O_3 

121 pm

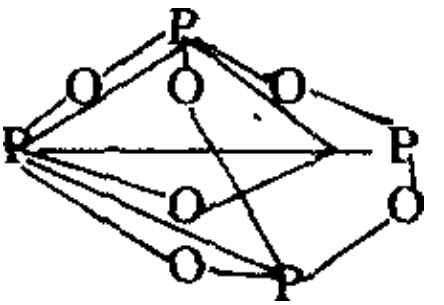
(iv) NO_2

(v) N_2O_4 

121 pm

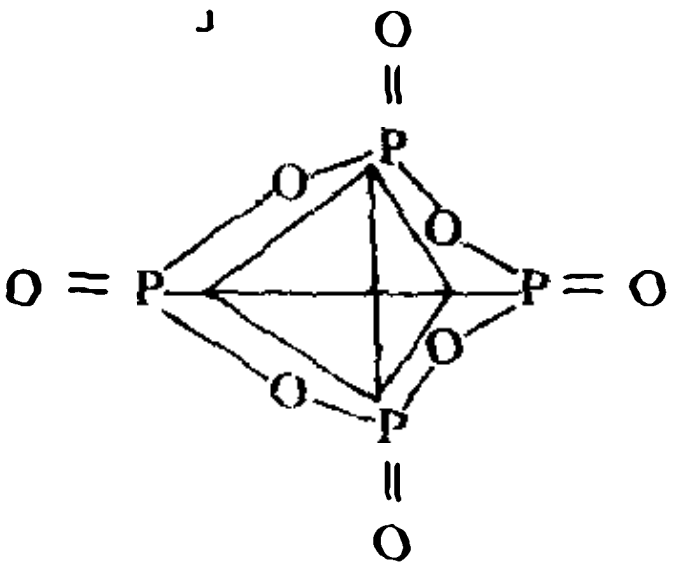
(vi) N_2O_5 

Structures of Oxides of Phosphorus :

(i) P_4O_6 

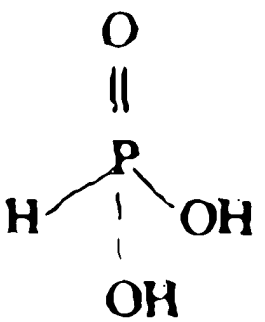
Phosphorus trioxide

(ii) P_4O_{10} Phosphorus pentaoxide

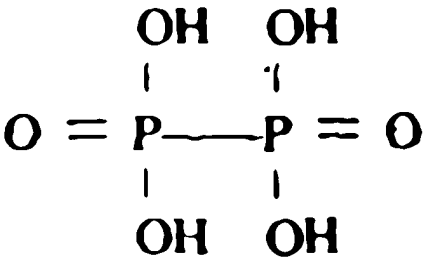


Structures of Oxyacids of Phosphorus

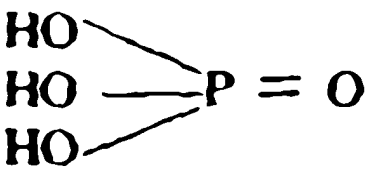
(i) Phorphorus acid H_3PO_3



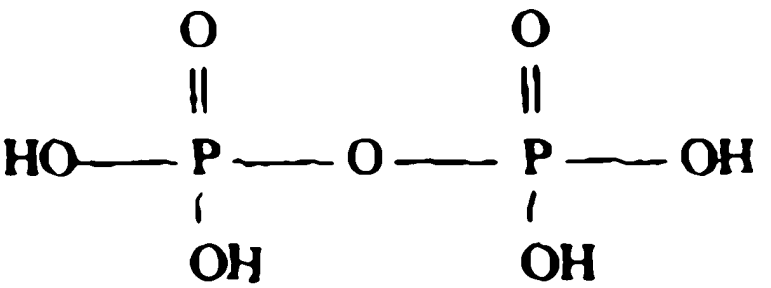
(ii) Hypophosphoric acid, $H_4P_2O_6$



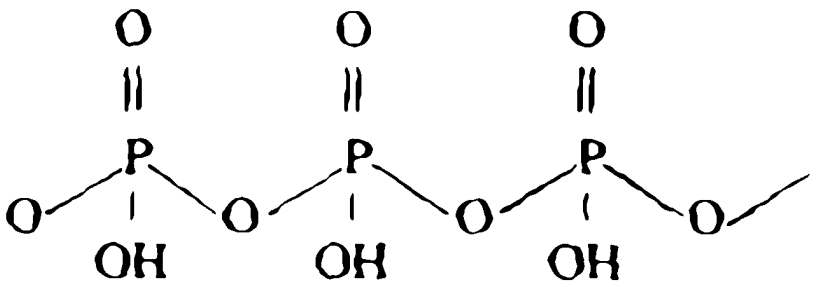
(iii) Orthophosphoric acid, H_3PO_4



(iv) Pyrophosphoric acid, $H_4P_2O_7$



(v) Polymetaphosphoric acid, $(HPO_3)_n$



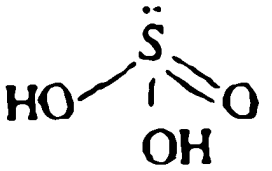
Uses of Phosphorus : It is used (i) in the manufacture of many organic and inorganic phosphates (phosphate manures).

(ii) in medicines to meet out the deficiency of phosphorus in diet for stimulating secretion of gastic juice. This stimulates appetite and improves digestion.

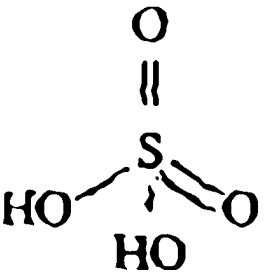
Group VI Elements (Oxygen Family) : O, S, Se, Te and Po are the elements of this group. The last member of the group. i.e. Polonium is radioactive. The electronic configuration of the valency shell of these elements is ns^2np^4.

Sulphur forms six oxyacids which are shown below :

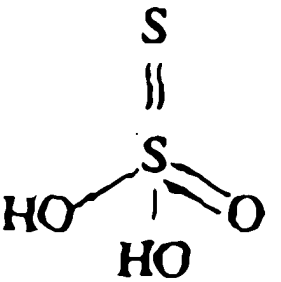
(i) Sulphurous acid, H_2SO_3



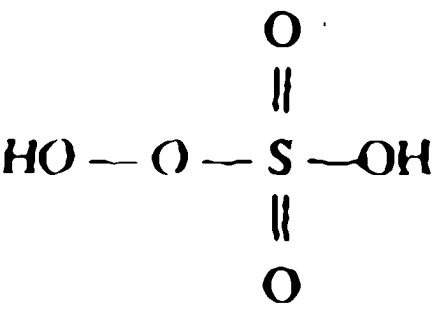
(ii) Sulphuric acid, H_2SO_4



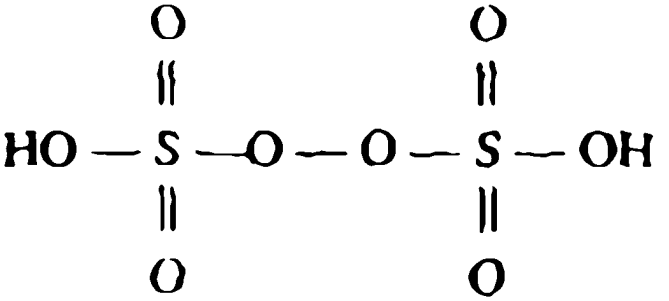
(iii) Thiosulphuric acid, $H_2S_2O_3$



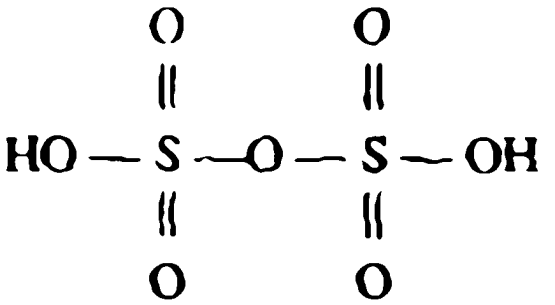
(iv) Peroxy mono sulphuric acid, H_2SO_5



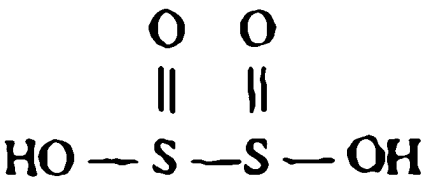
(v) Peroxydisulphuric Acid, $H_2S_2O_8$



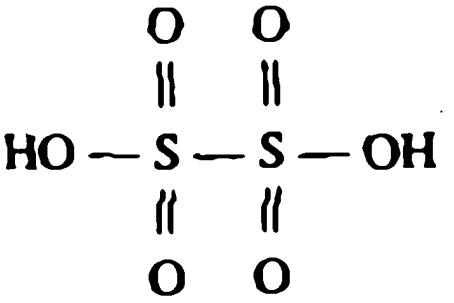
(vi) Pyrosulphuric acid, $H_2S_2O_7$



(vii) Dithionous acid, $H_2S_2O_4$



(viii) Dithionic acid, $H_2S_2O_6$



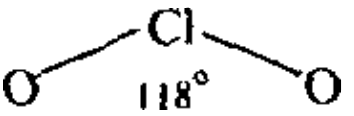
Group VII Elements (Halogen family) : This group contains five elements i.e., F, Cl, Br, I and At. The general electronic configuration of their outermost orbit is $ns^2\ np^5$.

Halogens form a number of oxides some of which and their structures are given below :

(i) Cl_2O

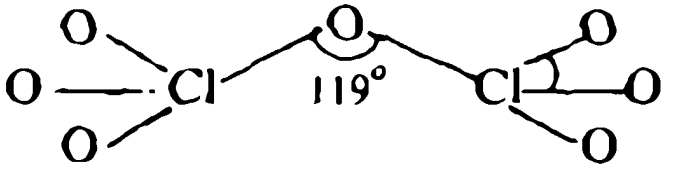
170 pm

(ii) ClO_2



147 pm

(iii) Cl_2O_7 141 pm 115°



Bromine and iodine also form oxides Br_2O, BrO_2 and I_2O_3 and I_2O_5 respectively.

All oxides are powerful oxidising agents and decompose explosively when subjected to mechanical vibrations or heat.

Following are the oxyacids of halogens formed in different oxidation states.

Oxyacid	Formula	Oxidation state of Cl
Hypochlorous acid	HClO	+1
Chlorous acid	$HClO_2$	+3

Oxyacid	Formula	Oxidation state of Cl
Chloric acid	$HClO_3$	+5
Perchloric acid	$HClO_4$	+7

It has been observed that with an increase in the oxidation state of chlorine there is an increase in the strength of the acid and also an increase in the thermal stability but a decrease in the oxidising power.

Acidic strength of hypohalous acids decreases in the order

HClO > HBrO> HIO

Thermal stability of hypohalous acids also decreases in the following order :

HClO > HBrO> HIO

Interhalogen Compounds : Compounds formed by the combination of two halogens are known as interhalogen compounds. In such compounds less electronegative

halogen is written first and it functions as electropositive element. Following are the different interhalogen compounds :

ClF, ClF_3, ClF_5, BrF, BrF_3, BrF_5, IF_3, IF_5, IF_7 etc.

Zero Group Elements (Noble Gases) : This group consists of He, Ne, Ar, Kr, Xe and Rn i.e. six elements. The general electronic configuration of the outermost orbit of these elements is ns^2p^6 (except for He which has $1s^2$). They are inactive and show no tendency to lose or gain electrons and are, therefore, known as inert gases.

Only weak Vander Waals forces are present between the atoms of noble gases in liquid or in solid state. These Vander Waals forces increase with size of the atoms and so their m.p. and b.p. increase from He to Rn.

Hydrogen : It is unique element which possesses metallic as well as non-metallic properties, therefore, it has been placed with

the alkali metals of I group as well as with halogens in VII group.

Isotopes of Hydrogen : *Hydrogen* has following three isotopes :

(a) Protium (H) $_{1}^{1}H$

(b) Deuterium (D) $_{1}^{2}H$

(c) Tritium (T) $_{1}^{3}H$

Transition Metals : Elements placed in between s-block and p-block elements in the periodic table are known as transition elements. These elements function as a bridge in between the strongly electropositive s-block and strongly electronegative p-block elements. They fall under two categories : (i) d-block or transition elements, and (ii) f-block or inner transition elements.

(i) d-block or Transition Elements : These are the elements in which *d*-orbital of the penultimate shell is partly filled while s-orbital of the ultimate shell is already filled with one or two electrons. They possess

$(n-1)d^{1-10}ns^{1-2}$ general electronic configuration in their valency shell. They fall under the following four series :

(a) First transition series—elements from atomic number 21 (Sc) to 30 (Zn) i.e. 3d series.

(b) Second transition series—elements from atomic number 39 (Y) to 48 (Cd) i.e., 4d series.

(c) Third transition series—elements from atomic number 57 (La) then from 72 (Hf) to 80 (Hg) i.e. 5d series.

(d) Fourth transition series—elements with atomic number 89 (Ac), 104 (Ku) and Ha (105) onwards i.e., 6d series.

Most of the d-block (transition) elements are paramagnetic in nature due to presence of unpaired electrons.

The paramagnetism is given by

Magnetic moment, $\mu = \sqrt{n(n+2)}$ B.M.

where n = number of unpaired electrons.

Most of the d-block elements, their ions or compounds exhibit colours which depend upon the promotion of electrons from lower d to higher d within the same d-sublevel. This is known as d-d transition.

d-block elements have an exceptional capacity of forming complex compounds. This is attributed to the smaller size of their ions and availability of vacant d-orbitals.

f-block or Inner Transition Elements. : Elements in which the f-sublevel of the antepenultimate shell is progressively filled while the d-sublevel of the penultimate shell is partly filled and s-sublevel of the ultimate shell has the required number of electrons. The general electronic configuration of these elements is given as $(n-2)\,f^{1-14}$ $(n-1)\,d^{1}ns^{2}$. These elements fall under two series (i) from atomic number 58 (Ce) to 71 (Lu) known as Lanthanides and (ii) from atomic number 90 (Th) to 103 (Lw) known as Actinides.

Both these series are placed at the bottom of periodic table to avoid sidewise expansion.

Lanthanide Contraction : In case of lanthanides there occurs a decrease in the atomic/ionic radii as we go from La/La^{3+} to Lu/Lu^{3+}. This phenomenon of decrease in atomic/ionic radii is called lanthanide contraction.

COMPLEXES OR COORDINATION COMPOUNDS

A complex or coordination compound is made up of a central metal surrounded by some simple ions or neutral molecules e.g. $\left[Co\,(NH_3)_3Cl_3\right]$

Ligands : The ions or molecules attached to the central metal are called ligands. Ligand is supposed to donate at least one lone pair of electrons to the central metal atom.

Coordination Number : It is the total number of ligands (ions or molecules) at-

tached to the central metal ion. It is also equal to the number of secondary valencies of the central metal. The most commonly encountered coordination number is 4 or 6.

Effective Atomic Number (EAN) : It is equal to the total number of electrons possessed by the central metal including those gained by coordination and lost in ion formation. Mathematically it can be expressed as :

EAN= Atomic number of central metal – electrons lost in ion formation + electrons gained by coordination.

Some complexes, their IUPAC names and their EAN are given below.

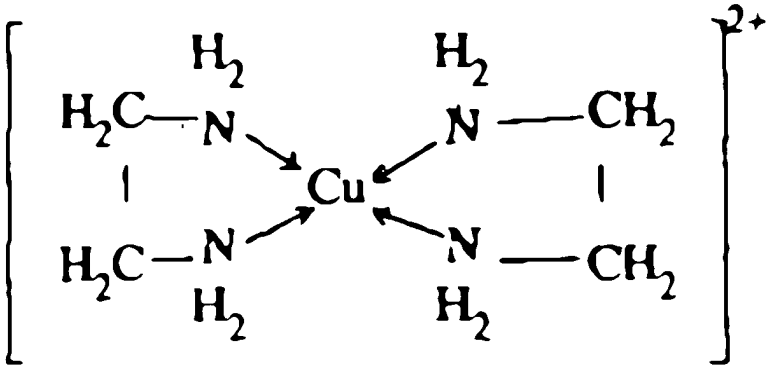
	Complex formula	IUPAC names	EAN
(a)	$[Co(NH_3)_3Cl_3]$	Trichloro-triammine cobalt (III)	27–3+12 = 36

	Complex formula	IUPAC names	EAN
(b)	$[Pt(NH_3)_6]Cl_4$	Hexamine Platinum (IV) chloride	78–4+12 = 86
(c)	$K_3[Fe(CN)_6]$	Potassium Hexacyano-ferrate (III)	26–3+12 = 35
(d)	$K_3[Fe(C_2O_4)_3]$	Potassium trioxalato-ferrate (III)	26–3+12 = 35

Complex Ion : It is an electrically charged radical formed by the combination of a central metal atom surrourded by a group of simple ions or neutral molecules. The charge on the complex ion is the algebraic sum of the charges possessed by the central metal ion and the ligands.

Chelate : Chelates are the ring structure complexes formed by a polydentate ligand

(ligand having more than one donor atom) with the central metal e.g.



Organometallic Compounds : These are the compounds which contain one or more metal-carbon bonds. The compounds of some metalloids such as boron and silicon are also included in this classification.

Classification of Organometallic Compounds :

(i) σ-bound compounds e.g. R–Mg–X, such as $(C_2H_5)_2Zn$, $(CH_3)_4Sn$, $M(CO)_4$

(ii) π-complexes e.g. zeisse's salt, ferrocene dibenzene chromium etc.

ORGANIC CHEMISTRY

ORGANIC CHEMISTRY

Organic chemistry is defined as the chemistry of the hydrocarbons (compounds having carbon and hydrogen) and their derivatives.

Organic compounds are characterised by inflammability, their insolubility in polar solvents, their non-ionic nature and covalent linkages etc. Plants, animals, coal, petroleum and oil etc. are the main sources of organic compounds.

Allotropy : It is the property by virtue of which an element can exist in two or more different forms in the same state. The different forms are known as allotropes or allotropic modifications.

The systematic way of naming the organic compounds is known as nomenclature. The most commonly used method of nomenclature is IUPAC (International Union of Pure and Applied Chemistry) method.

Hydrocarbons : Compounds which contain only carbon and hydrogen are called hydrocarbons e.g. CH_4, C_2H_6, C_3H_8, C_2H_4, C_2H_2, C_3H_4, C_3H_6, C_6H_6 etc.

General Classification of Organic Compounds : They have been classified as :

(i) Saturated and unsaturated compounds

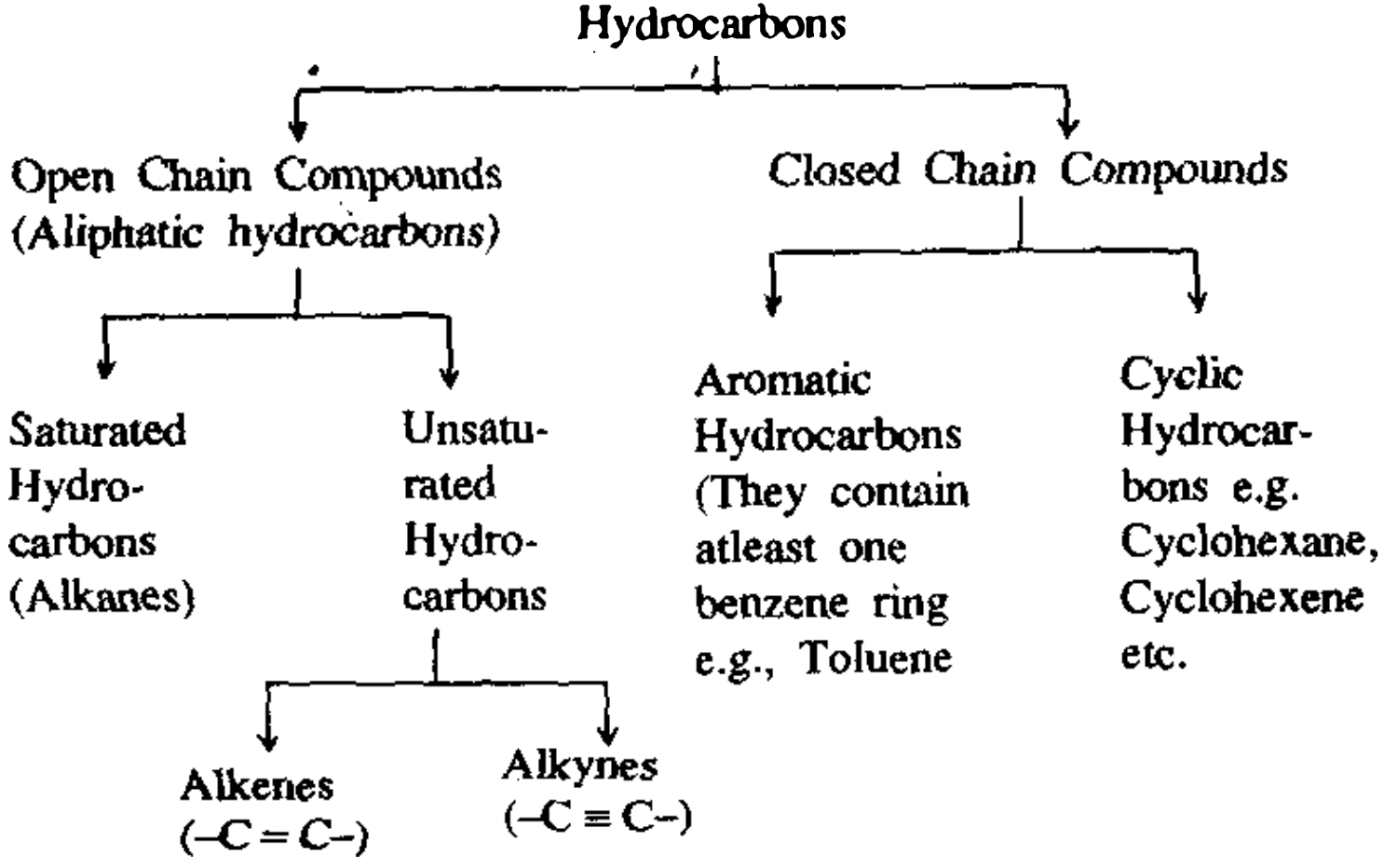
(ii) Aliphatic and aromatic compounds

(iii) Acyclic and cyclic compounds

(iv) Carbocyclic and heterocyclic compounds.

Hydrocarbons : They have been classified as follows :

Alkanes : These are saturated, open chain hydrocarbons e.g. CH_4, C_2H_6 etc. They are also called paraffins. They are given the general formula as C_nH_{2n+2}. They have C–C bonds. In these compounds the carbon atom is in sp^3 hybridised state.


Hydrocarbons
Open Chain Compounds
(Aliphatic hydrocarbons)
Closed Chain Compounds
Saturated Hydro-carbons (Alkanes)
Unsatu-rated Hydro-carbons
Aromatic Hydrocarbons (They contain atleast one benzene ring e.g., Toluene
Cyclic Hydrocar-bons e.g. Cyclohexane, Cyclohexene etc.
Alkenes (–C = C–)
Alkynes (–C ≡ C–)

Isomers : Organic compounds which have the same molecular formula but different structural formula are called isomers. Butane ((C_4H_{10}) has the two following isomers :

$$H_3C—CH_2—CH_2—CH_3$$

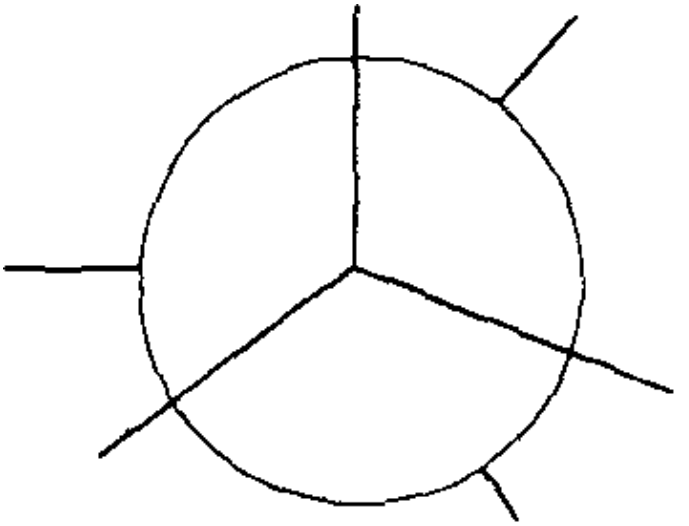
(n-butane)

and

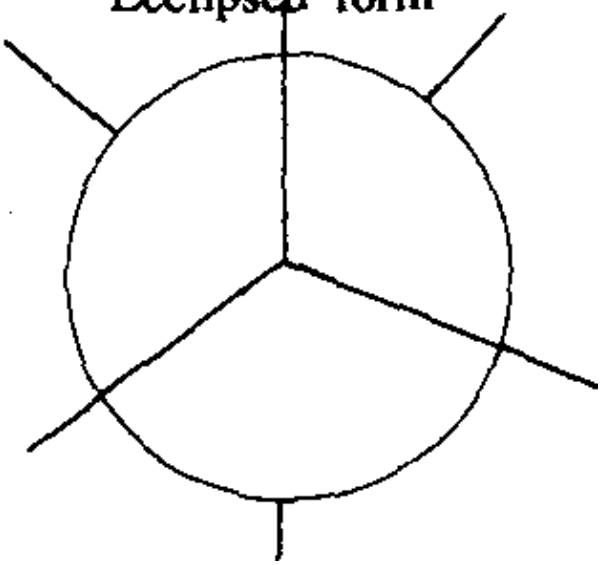
$$H_3C—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$$

(Isobutane or 2 methyl propane)

Conformations of Hydrocarbons : The different spatial arrangements that take place because of the rotation about a carbon-carbon single bond are known as conformations. The various structures which are obtained due to rotation about carbon-carbon single bond are called conformers. The two conformers of ethane are



Ecclipsed form



Staggered form or Anti-form

In between these two extreme, there are many other forms which are known as skew forms.

In eclipsed conformation the similar hydrogen atoms attached to the carbon atoms eclipse each other and the repulsion between them is maximum.

In staggered conformation the similar hydrogen atoms attached to two carbon atoms are at maximum distance apart and the repulsion between them is minimum.

Alkenes : These are unsaturated aliphatic hydrocarbons having atleast one carbon-carbon double bond in their molecule. They have the general formula C_nH_{2n}. Each carban atom involved in double bond is sp^2 hybridised. A double bond consists of one σ and one π bond e.g. C_2H_4, C_3H_6 etc.

Alkynes : These are also unsaturated alliphatic hydrocarbons which have atleast one carbon-carbon triple bond ($C \equiv C$). They possess the general formula C_nH_{2n-2}. The carbon atoms involved in triple bond formation are sp hybridised. A triple bond consists

of one σ- and two π-bonds e.g. C_2H_2, C_3H_4, C_4H_6 etc.

KINDS OF ISOMERISM

(i) Structural Isomerism :

$$H_3C - CH_2 - CH_2 - CH_2 - CH_3$$

n-propane (straight chain)

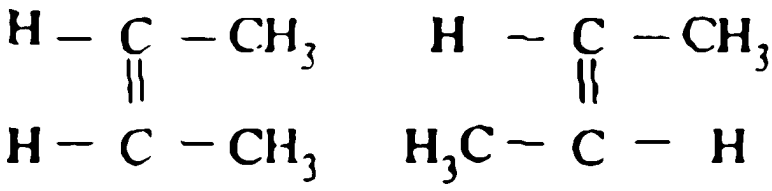
$$H_3C - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - CH_3$$

Isopropane (Branched chain)

(ii) Stereo Isomerism : Isomers which differ with respect to the arrangement of atoms or groups in space are said to be stereo isomers and the phenomenon is known as stereo isomerism. It is of two types (a) Geometrical isomerism, (b) Optical isomerism.

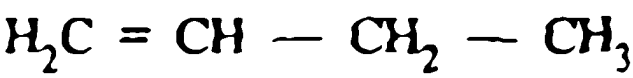
Geometrical Isomerism : This isomerism arises due to position of two similar groups about the same carbon-carbon double

bond. When similar groups are attached to the same side of the molecule, it is known as cis-isomer and when the two similar groups are on opposite sides of carbon-carbon double bond, the molecule is then known as trans-isomer, e.g.

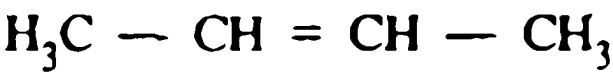


Cis-2-butene Trans-2-butene

Position Isomerism : This is caused by difference in position of the same group in the same chain, e.g.



1-butene

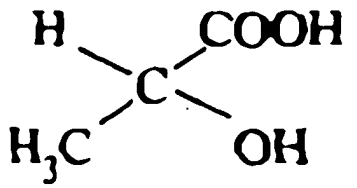


2-butene

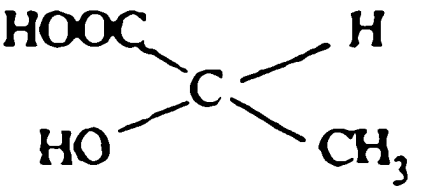
Optical Isomerism : This isomerism is shown by the compounds having at least one asymmetric (chiral) carbon atom.

An object which cannot be superimposed on its mirror image is known as chiral. Those objects which are superimposable on their mirror images are known as achiral.

Lactic acid exhibits optical isomerism and its two isomers are



(A)



(B)

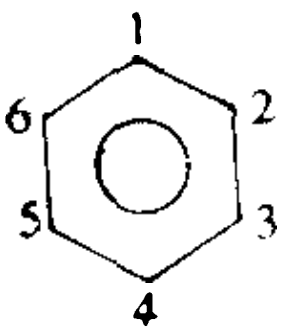
Stereo isomers differ only in their optical activity. One is dextro-rotatory and other (mirror image) is leavo-rotatory.

Isomerism in Arenes :

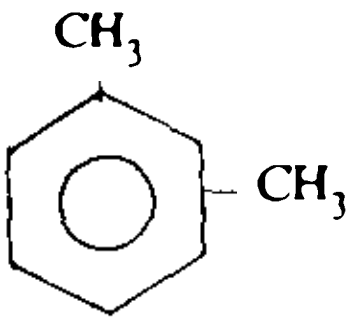
Arenes are the aromatic hydrocarbons e.g. C_6H_6, C_7H_8 etc. The simplest arene is benzene C_6H_6.

When the two substituent groups are attached to adjacent carbon atoms at 1 and 2 positions, it is called ortho-isomer.

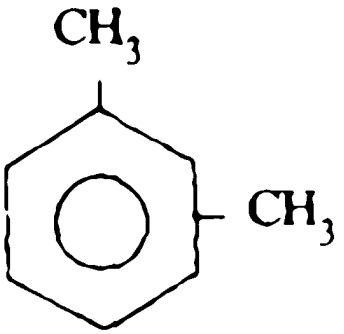
When the two substituent groups are attached to 1 and 3 carbon atoms, it is called a meta isomer and when the two substituent groups are attached to 1 and 4 carbon atoms, it is called a para isomer.



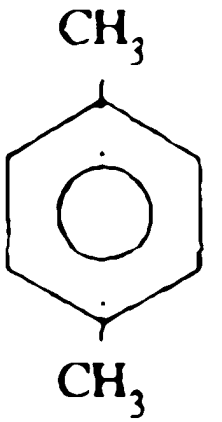
Benzene



Ortho –



Meta –



Para –

VARIETIES OF ORGANIC REACTIONS

(i) Addition Reaction :

$$H_2C = CH_2 + H_2 \xrightarrow{Ni} H_3C - CH_3$$

Ethane

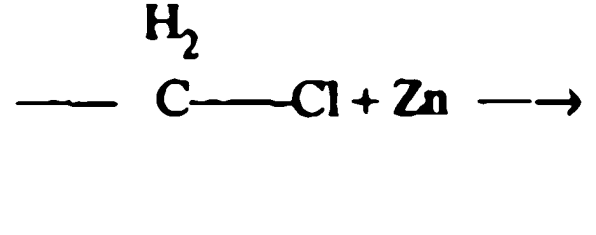
(ii) Substitution Reaction :

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + Cl_2$$

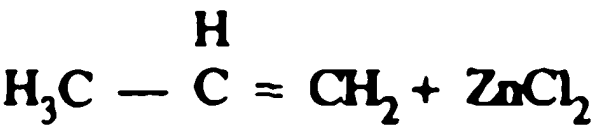
$$\rightarrow CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + Cl_2$$

$$\longrightarrow CCl_4$$

(iii) Elimination Reaction :



1,2- dichloropropane



1-propene

Organic compounds possess the following common characteristics.

(i) **Group or Radical :** Organic compounds may be considered to be made up of two parts. Each part or group is known as a radical e.g. $C_2H_5NH_2$ consists of ethyl ($-C_2H_5$) radical and amino ($-NH_2$) radical.

(ii) **Functional Group :** It is that part of the organic compound which determines its properties e.g. –OH is the functional group for alchols (R–OH). Many other characteristic functional groups are :

Group	*Class of Compound*
–F, –Cl, –Br, –I (Halo)	Halides (Fluoride, Chloride, Bromide, Iodide)
–OH (Hydroxy)	(i) alcohols (ii) Phenols

Group	Class of Compound
C=O (Carbonyl)	(i) Aldehydes $-C(=O)-H$ (ii) Ketones C=O
$-C(=O)-OH$ (Carboxyl)	Carboxylic acids
$-NH_2$	Amines (Primary)
>NH	Amines (Secondary)
N	Amines (Tertiary)
-O-	Ether
$-C(=O)-O-$	Ester

Group	Class of Compound
$-C(=O)-NH_2$	Amide
$-NO_2$	Nitro-derivative
$-NO$	Nitroso-derivative
$-S-$	Sulphides or thio-ethers
$-SO_2$	Sulphones
$-SH$	Thiol
$-N=N-$	Diazo compounds
$-CN$	Cyanide, Nitriles
$-NC$	Isocyanide, Isonitriles

Alkanes : They have the general formula C_nH_{2n+2}. Following are the members of the series.

CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane

The next higher members are named using –ane suffix to the number of carbon atoms present in the molecule of alkane e.g. C_5H_{12} has five carbon atoms and is therefore named pentane. Similarly C_6H_{14} is named as hexane since it has six carbon atoms in the molecule.

IUPAC rules are followed for naming side chain hydrocarbons.

Alkyl Radical (R) : Alkyl radical is obtained by removing one hydrogen atom from the alkane, e.g.

CH_4 (Methane) $-CH_3$ (Methyl)

C_2H_6 (Ethane) $-C_2H_5$ (Ethyl)

Alkyl radical is given a general formula C_nH_{2n+1}.

The name of alkyl radical is derived by replacing the suffix-ane of alkane by -yl.

Alkenes : The name of alkene is given by changing the suffix-ane of the corresponding alkane by -ene.

C_2H_6 (Ethane) C_2H_4 (Ethene)

C_3H_8 (Propane) C_3H_6 (Propene)

Alkynes : The name of an alkyne is obtained by changing the suffix -ane of the corresponding alkane by -yne.

C_2H_6 (Ethane) C_2H_2 (Ethyne)

C_3H_8 (Propane) C_3H_4 (Propyne)

SOURCES OF HYDROCARBONS

Coal and Petroleum : Coal mainly consists of carbon. Different forms of coal contain the following percentage of carbon :

Anthracite	90% carbon
Bituminous	70% carbon
Lignite	40% carbon
Peat	10.19% carbon

Petroleum is a mixture of different hydrocarbons particularly alkanes, cycloalkanes and aromatic hydrocarbons.

Natural Gas : The main constituents of natural gas are methane, ethane, propane and butane.

Marsh Gas : It is also known as Methane.

COMPONENTS OF COAL TAR

(i) **Neutral Components :** Benzene, toluene, xylene, naphthalene and anthracene.

(ii) **Basic Components** : Pyridine, quinoline etc.

(iii) **Acidic Components** : Phenols, cresols etc.

Refining (Processing) of Petroleum : It means to carry out continuous fractional distillation of crude oil into different useful fractions and the removal of undesirable impurities.

Cracking : It is a process of decomposing higher hydrocarbons of the petroleum fraction into lower hydrocarbons with low boiling points by strong heating, e.g.

$$\underset{\text{Decane}}{H_3C-(CH_2)_8-CH_3} \xrightarrow{770\,k} \underset{\text{Octane}}{C_8H_{14}} + \underset{\text{Ethane}}{H_2C-CH_2}$$

Different Methods of Cracking : Following are the four methods of cracking.

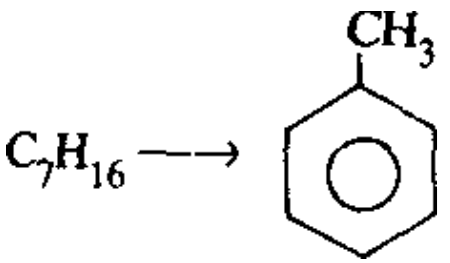
(i) Vapour phase cracking, (ii) Liquid phase cracking, (iii)Catalytic cracking, (iv) Steam cracking.

Polymerisation : *It is a process in which* small molecules combine together to form bigger molecules

$$n.H_2C = CH_2 \longrightarrow (H_2C = CH_2)_n$$

Polymer

Reforming : The process of conversion of aliphatic or alicyclic hydrocarbons into aromatic hydrocarbons in the presence of a suitable catalyst such as platinum, nickel or palladium is known as reforming or Aromatisation. e.g.



(n-heptane) (toluene)

Knocking : The sudden and irregular burning of fuel mixture that causes gerk against the piston and gives rise to violent sound is known as knocking.

Octane Number : This is used to know about anti-knock quality of the fuel.

Octane number zero n-heptane.

Octane number 100 - ISO octane (2, 2, 4-Trimethyl pentane).

Octane number can be defined as the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane which has the same anti-knock qualities as the fuel under test.

Gasoline Additives are added to gasoline to decrease knocking. The compounds which are added to gasoline to improve its octane number are called **anti-knocking agents.** Tetra-ethyl lead (TEL), $(C_2H_5)_4Pb$ is the best known anti-knocking agent. Gasoline containing TEL is known as ethyl gasoline or leaded gasoline.

Preparation of Hydrocarbons :

Alkanes : (i) Sabatier and Sanderen's reaction.

From unsaturated hydrocarbons

$$H_2C = CH_2 + H_2 \xrightarrow[\text{or pt}]{Ni} H_3C{-}{-}CH_3$$

(ii) From alkyl halides

(a) Wurtz Reaction

$$2C_2H_5I + 2Na \xrightarrow{ether} C_4H_{10} + 2NaI$$

(b) Using Grignards reagent

$$CH_3CH_2Br + Mg \xrightarrow[ether]{diethyl} \underset{\text{Grignard's reagent}}{CH_3CH_2MgBr}$$

$$CH_3CH_2MgBr + H_2O \rightarrow C_2H_6 + Mg\begin{matrix}Br\\OH\end{matrix}$$

(c) Reduction of alkyl halides

$$C_2H_5Br + 2HI \longrightarrow C_2H_6 + HBr + I_2$$

(iii) From carboxylic acids

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

$$CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$$

(iv) Electrolytic Method (Kolbe's Method)

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

$$CH_3COO^- \longrightarrow CH_3^- + CO_2$$

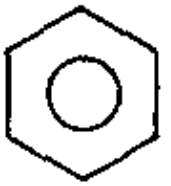
$$CH_3 + CH_3 \longrightarrow C_2H_6$$

Alkenes : (i) From Halides

$$CH_3CH_2CH_2Br + KOH \xrightarrow[360\ K]{\text{Ethenol}} CH_3CH = CH_2 + KBr + H_2O$$

(ii) From Alcohols

$$\xrightarrow[373\text{-}383\ K]{H_3PO_4}$$



$$+ H_2O$$

cyclohexene

$$C_2H_5OH \xrightarrow[630\ K]{Al_2O_3} H_2C = CH_2 + H_2O$$

Alkynes : They are prepared by the action of water on calcium carbide

$$CaC_2 + H_2O \longrightarrow \underset{\text{Ethyne}}{C_2H_2} + Ca(OH)_2$$

Properties (Chemical)

Alkanes : (i) Substitution

$$CH_4 \xrightarrow[-HCl]{Cl_2} CH_3Cl \xrightarrow[-HCl]{Cl_2} CH_2Cl_2$$

$$\xrightarrow[-HCl]{Cl_2} CHCl_3 \xrightarrow[-HCl]{Cl_2} CCl_4$$

(ii) Combustion

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

(iii) Oxidation (Controlled)

$$CH_4 \xrightarrow[Cr_2O_3]{O_2} CH_3OH \quad \text{(methanol)}$$

Alkenes :

(i) Substitution :

$$H_2C = CH_2 + Cl_2 \xrightarrow{770\ K} H_2C = CHCl$$

(Vinyl Chloride)

(ii) Addition :

$$H_2C = CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2 - CH_2Br$$

(iii) Oxidation :

$$H_2C = CH_2 + O_2 \xrightarrow[Ag]{620\ K} \underset{\underset{(epoxyethene)}{O}}{H_2C - CH_2}$$

(iv) Combustion :

$$H_2C = CH_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

Alkynes :

(i) Addition Reaction :

$$HC \equiv CH \xrightarrow{Ni} H_2C = CH_2 \xrightarrow{H_2} CH_3 - CH_3$$

(ii) Oxidation :

$$HC \equiv CH \xrightarrow{KMnO_4/H_2O} HOOC - COOH$$

(iii) Combustion :

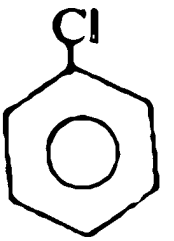
$$2(HC \equiv CH) + 5O_2 \longrightarrow 4CO_2 + 2H_2O$$

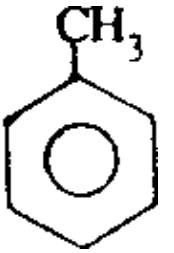
Arenes :

(i) Addition Reaction :

$$C_6H_6 + Cl_2 \xrightarrow{\text{sunlight}} C_6H_6Cl_6$$

(ii) Substitution

$$C_6H_6 + Cl_2 \xrightarrow[\text{dark}]{FeCl_3}$$ 

$$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3}$$ 

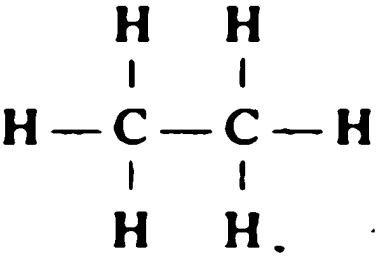
(iii) Combustion

$$C_6H_6 + O_2 \xrightarrow{\text{Burn}} 6CO_2 + 3H_2O$$

STRUCTURES OF HYDROCARBONS

Alkanes : Specific example of ethane, C_2H_6

The two carbon atoms are bonded to one another and to the hydrogen atoms by 6-bonds. i.e.



Alkenes : Specific example of Ethylene, C_2H_4.

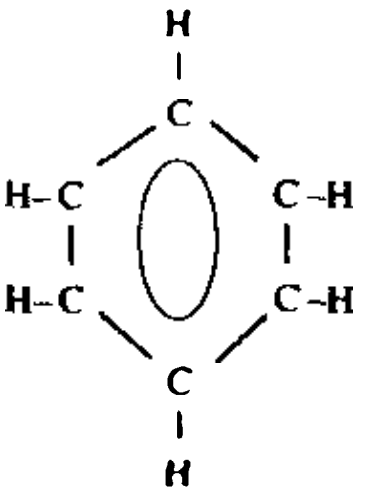
Here in C_2H_4, the two carbon atoms are bonded to each other by a σ-bond and also by a π bond i.e. by a double bond. The hydrogen atoms are bonded to carbon by σ bonds. $H_2C = CH_2$

Alkynes : Specific example of acetylene, C_2H_2.

In acetylene the two carbon atoms are bonded to each other by one σ and two π bonds i.e. by a triple bond. The hydrogen atoms are bonded to the carbon by σ bonds. Thus the structure can be shown as

$$H—C \equiv C—H$$

Structure of Benzene : The six carbon atoms are having sp^2 hybridisation. The six 2p-non-hybridised orbitals fuse together to form a delocalised electron cloud above and below the plane of the ring.



C-H bond length=1.09 Å

C-C bond length=1.39 Å

Bond angles = 120^0

1 Å =1 Angstrom = 10^{-10} metres.

Resonance : When several structures are assumed to contribute to the true structure of a molecule, but none of them can be said

to represent it completely, the molecule is referred to as resonance hybrid and the process is known as resonance.

Conditions for Resonance :

(i) The arrangement of atoms of a compound must be identical of almost identical for every formula.

(ii) The energy contents of all the canonical forms must be nearly equal.

(iii) The number of unpaired electrons in each canonical form must be the same.

Markownikoff's Rule : When addition occurs between a hydrogen halide and an unsymmetrical multiple bond, the halogen atom is attached to the carbon atom with the least number of hydrogen atoms.

$$H_3C - CH = CH_2 = HBr \longrightarrow \underset{\displaystyle H_2C - \overset{\displaystyle H}{\overset{|}{C}} - CH_3}{\underset{|}{Br}}$$

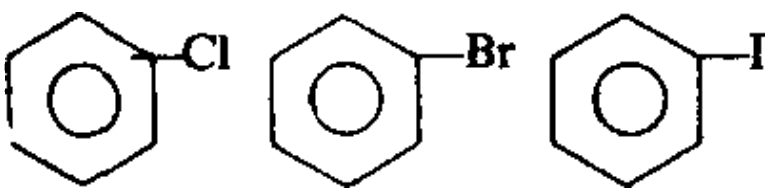
ALKYL AND ARYL HALIDES

Alkyl halides also known as Halo-alkanes possess the general formula RX, where R is alkyl group (C_nH_{2n+1}) and X is Cl, Br, I.

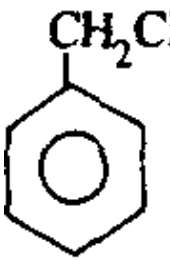
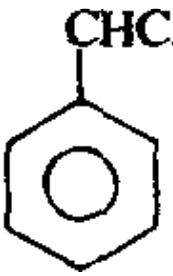
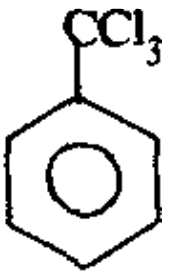
They can be classified as primary, secondary or tertiary alkyl helides depending on the fact whether halogen atom is attached to a primary, secondary or a tertiary carbon atom.

Aromatic Halogen Compounds

(a) **Aryl Halides** : In these halides halogen atom is directly linked to carbon atom of benzene nucleus. e.g.



(b) **Side Chain substitution derivatives e.g. :**

METHODS OF PREPARATION

Haloalkanes

(i) From Alkanes

$$H_3C.CH_2.CH_3 \xrightarrow[light]{Cl_2} CH_3CH_2Cl + CH_3Cl$$

(ii) From Alkenes

$$H_2C = CH_2 + HCl \longrightarrow H_3C.CH_2Cl$$

(iii) From Alcohols

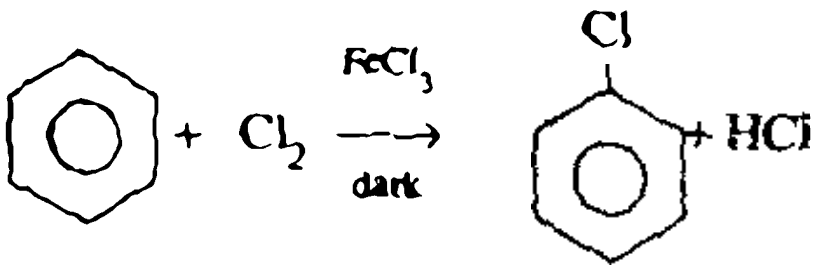
$$3\,CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$

(iv) From Silver Salts of Fatty Acids

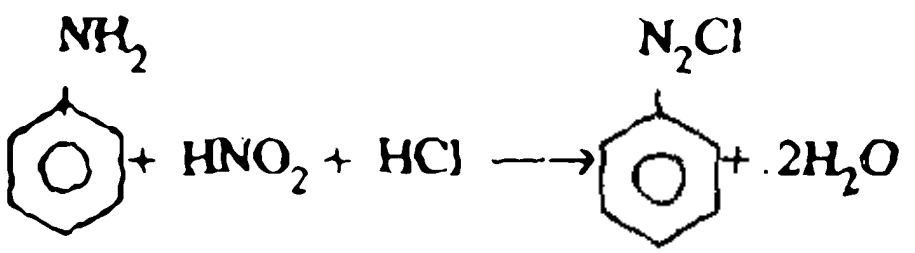
$$CH_3CH_2COOAg + Br_2 \xrightarrow{CCl_4} CH_3CH_2Br + AgBr + CO_2$$

Haloarenes

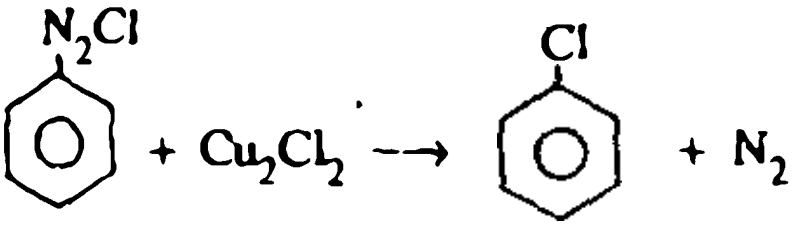
(i) By *direct halogenation*



(ii) From *Diazonium* Compounds



Benzene diazonium chloride



(Sand Meyer's Reaction)

If copper powder and HCl or HBr are used in the reaction of diazonium salt then the reaction is known as Gatterman's reaction and not the sand Meyer's reaction.

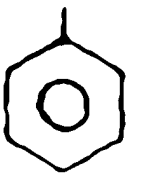
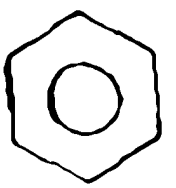
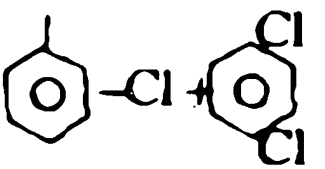
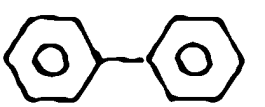
Chemical Properties :

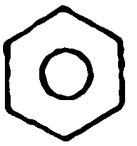
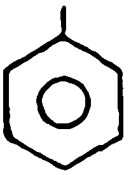
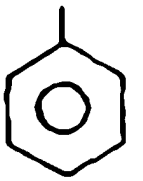
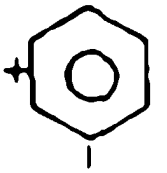
Alkyl Halides :

C_2H_5Br	Aq. KOH	C_2H_5OH
	KNO_2	C_2H_5ONO
	$AgNO_2$	$C_2H_5NO_2$
	NH_3	$C_2H_5NH_2$

	$NaSCH_3$	$C_2H_5SCH_3$
	Alc. KOH	$H_2C = CH_2$

Haloarenes

	$NH_3.Cu_2O$	NH_2 
	$Cl_2/FeCl_3$ 	Cl 
	Na	

	Na / CH_3Cl 	CH_3 
	$Na—Al/NaOH$	
	HNO_2 / H_2SO_4	Cl  $-NO_2$ Cl  NO_2

Poly Halogen Derivatives :

Haloforms : Chloform ($CHCl_3$), Bromoform ($CHBr_3$) and Iodoform (CHI_3).

Reactions of Haloforms

	HI/P_4	CH_2I_2
CHI_3	Air, Moisture, Δ	$I_2 + CO_2 + H_2O$
	$AgNO_3$ Δ	AgI

Chloretone, $H_3C-\underset{\displaystyle CCl_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$, is used as a sleep inducing drug (Hypnotic).

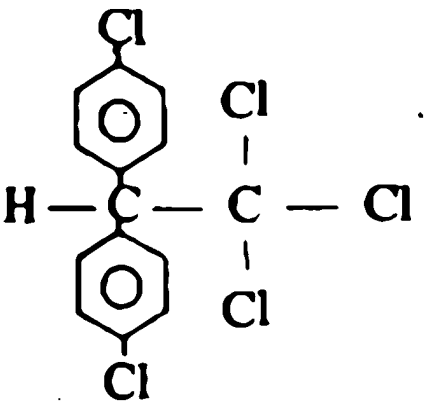
Chloropicrin, CCl_3NO_2 is used as an insecticide and war gas.

Carbon Tetrachloride, CCl_4

It is widely used as a solvent and as a fire extinguisher under the name pyrene.

Dichlorodifluoro Methane (Freon) CCl_2F_2 : It is used as a refrigerant and propellant in aerosols.

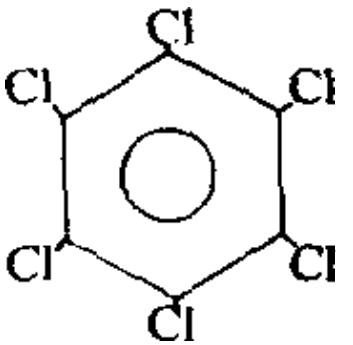
D.D.T. [2, 2,-bis (p-chlorophenyl)-1, 1, 1-trichloro ethane] $[(C_6H_4Cl)_2.CH.CCl_3]$: It is a white powder with a fruity smell. It is used as a contact insecticide.



(D.D.T)

Dichloro Diphenyl trichloro ethane.

Benzene Hexachloride (BHC) : It is used as pesticide in agriculture under the trade name gammexane.



(Hexachlorocyclohexane)

Westrol (Trichloroethylene), $CHCl—CCl_2$: It is used as a catalyst. It is prepared by heating westron $CHCl_2 — CHCl_2$ and $BaCl_2$.

ALCOHOLS AND PHENOLS

Functional group –OH

General formula for alcohol—ROH

General formula for phenols–ArOH (*–OH is attached to aromatic ring*)

Methods of Preparation

Alcohols :

(i) Hydration of alkenes

$$CH_2 = CH_2 + H_2SO_4 \longrightarrow$$

$$CH_3CH_2HSO_4 \xrightarrow[-H_2SO_4]{H_2O} CH_3CH_2OH$$

(ii) Hydrolysis of Haloalkanes

$$RX + \text{aq. KOH} \longrightarrow ROH + KX$$

(iii) From Aldehydes and Ketones

(a) By *reduction*

$$CH_3CHO + 2H \xrightarrow{LiAlH_4} CH_3CH_2OH$$

$$CH_3COCH_3 + 2H \xrightarrow{LiAlH_4} CH_3\,CH_3\,CHOH$$

(b) Using Grignard's Reagent

$$HCHO + CH_3MgBr \longrightarrow CH_3CH_2OH$$

Primary alcohol

$$+ \quad Mg\begin{matrix}OH\\Br\end{matrix}$$

$$CH_3CHO + CH_3MgBr \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH - OH$$

Secondary alcohol

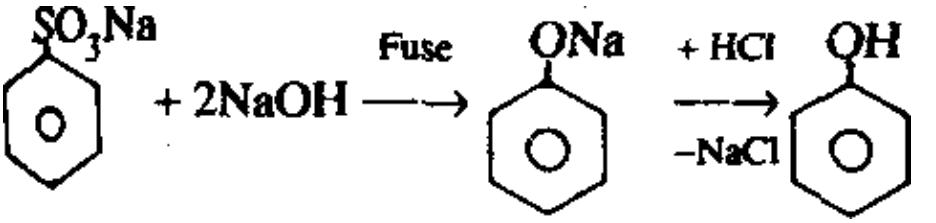
$$CH_3COCH_3 + CH_3MgBr \longrightarrow$$

$$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!\!>\!C - OH$$

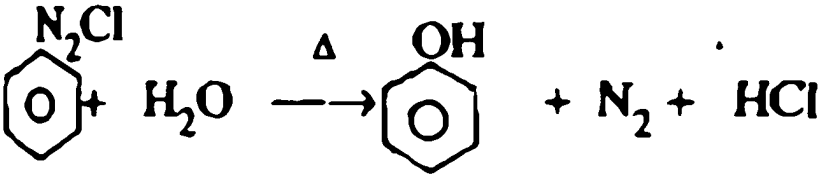
Tertiary alcohol

Phenols :

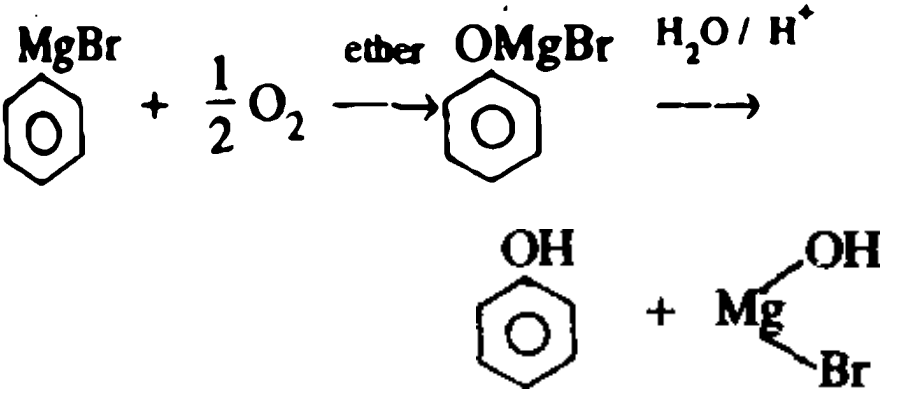
(i) Alkali fusion of sulphonates



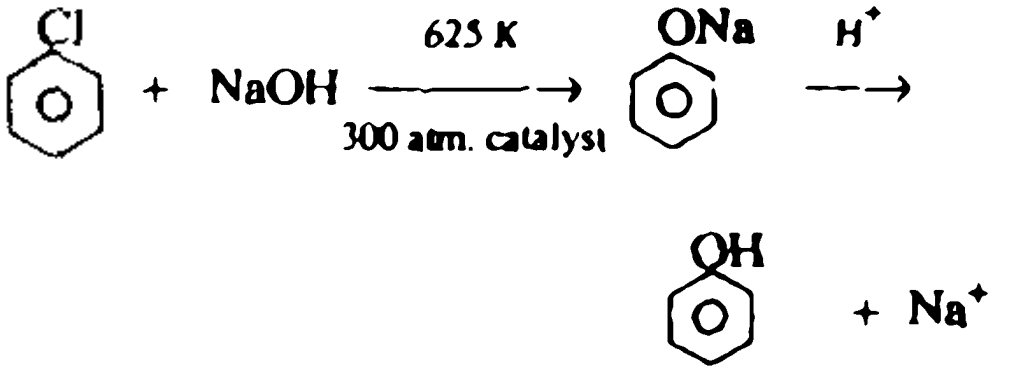
(ii) From diazonium salts



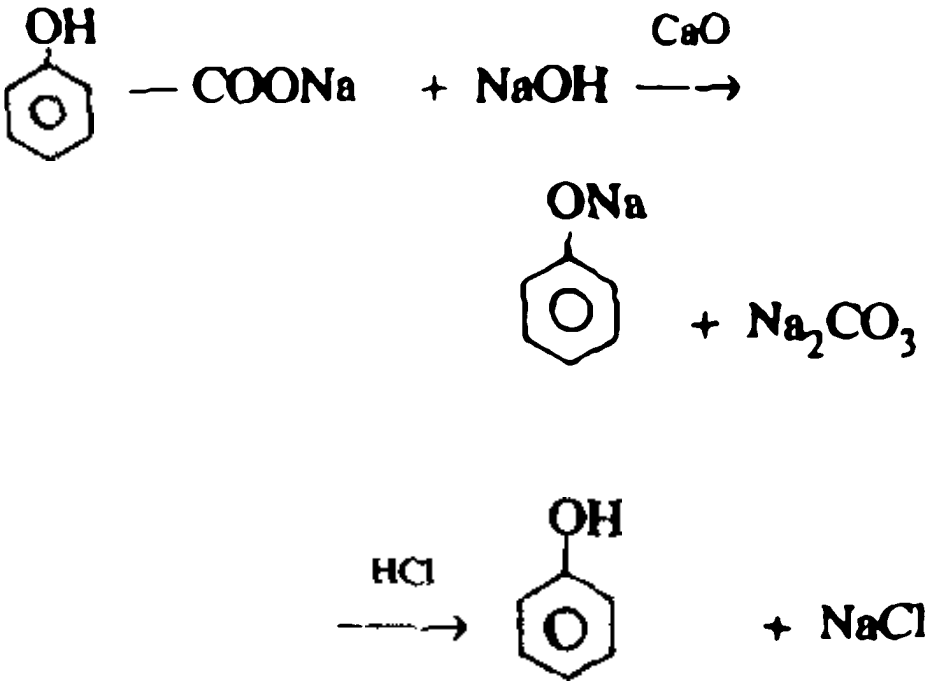
(iii) From Grignard's Reagent



(iv) From Aryl Halides (Dow's process)



(v) Phenol can be obtained by decarboxylation of sodium salt of salicylic acid.



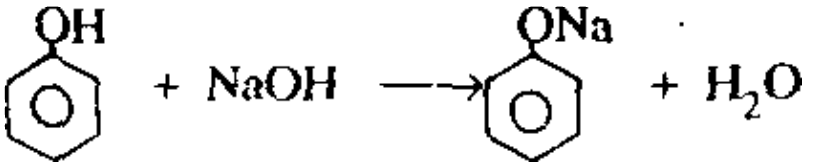
Chemical Properties :

Alcohols :

C_2H_5OH	Na	$C_2H_5ONa + H_2$
	PCl_5	C_2H_5Cl
	PX_3 (X = Cl, Br, I)	C_2H_5X
	$SOCl_2$	C_2H_5Cl
	CH_3COOH	$CH_3COOC_2H_5$
	CH_3COCl	$CH_3COOC_2H_5$
	$K_2Cr_2O_7$	CH_3COOH

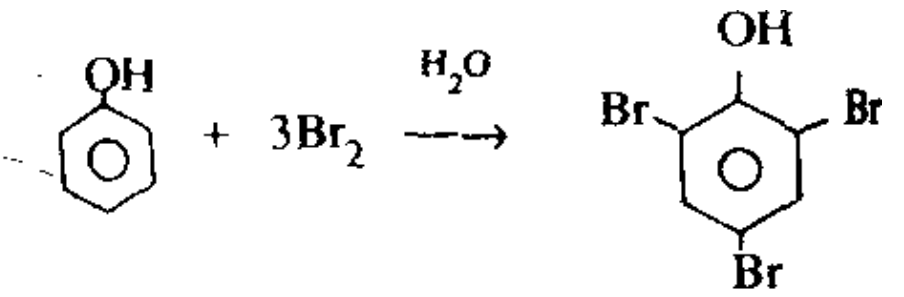
Phenols

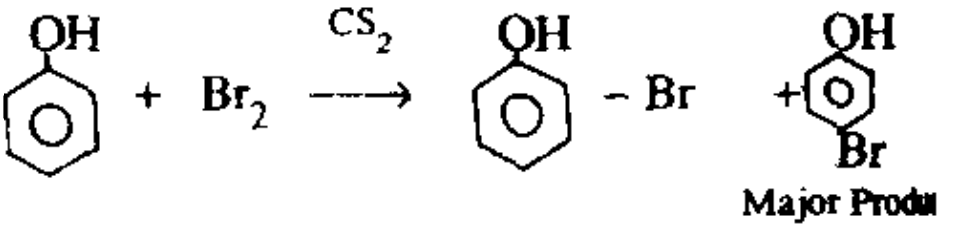
Acidic Properties : (i) Action with metals



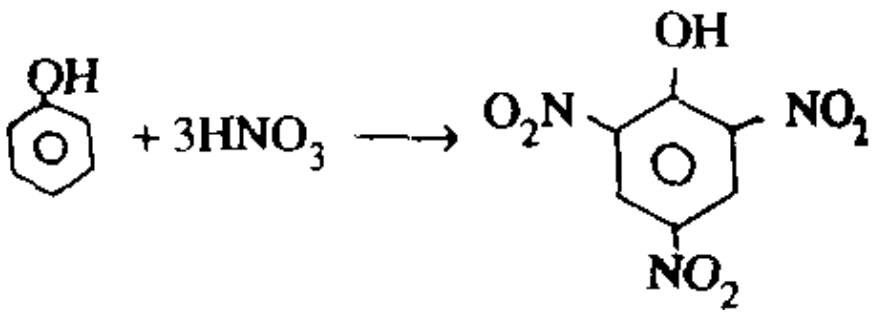
(ii) Phenols turn blue litmus into red.

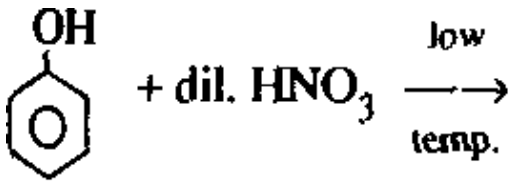
Substitution Reaction : (a) Halogenation

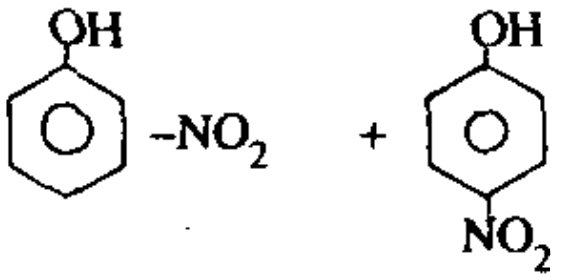




(b) Nitration :

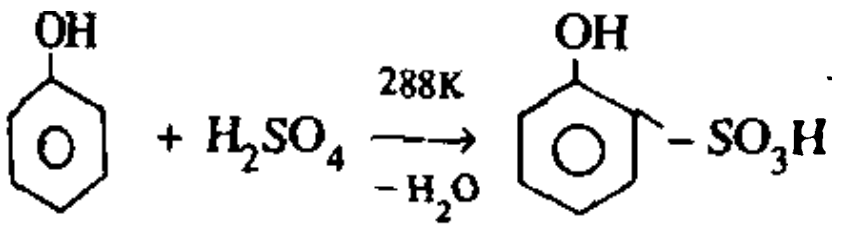


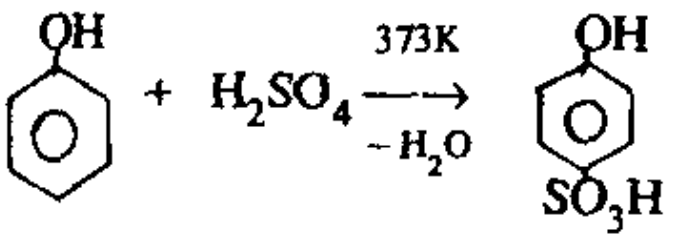




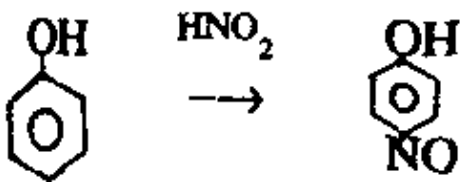
Major Product

(c) Sulphonation :

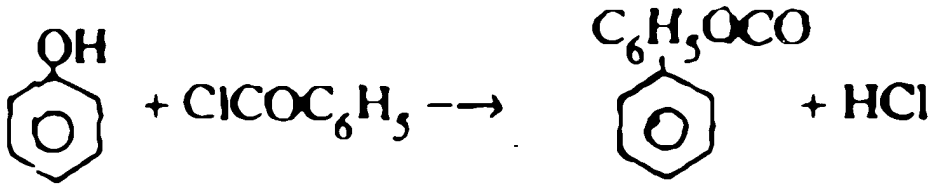




(d) Nitrosation :

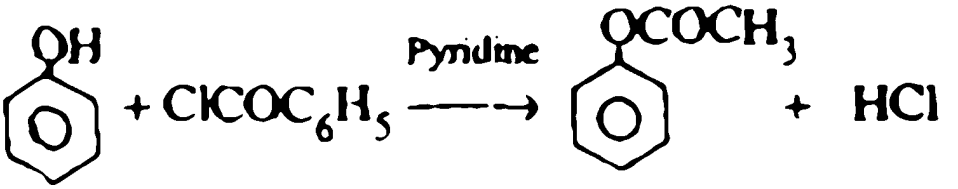


(e) Benzoylation :



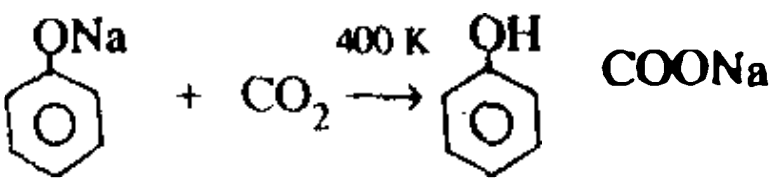
Phenyl Acetate

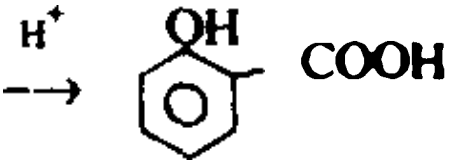
(f) Fridel-crafts Acylation :



Other Specific reations :

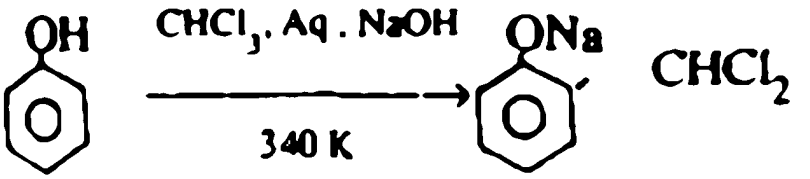
(i) Kolbe's Reaction

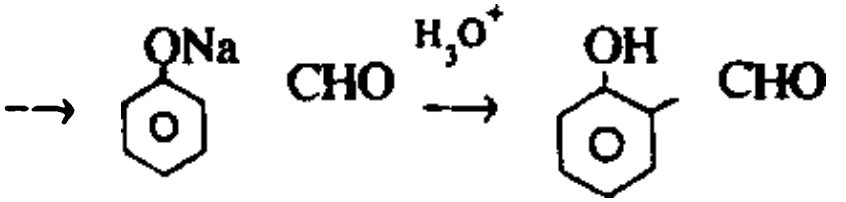




Salicylic Acid

(ii) Reimer-Tiemann Reaction





C_2H_5OH, Ethanol is known as grain alcohol. 95% ethanol (95% ethanol+5% water) is known as rectified spirit. Ethanol denatured by methanol is called methylated spirit. 100% ethanol is called absolute alcohol. Ethyl alcohol used for purpose of power generation in internal combustion engine is known as power alcohol.

Glycol : $(CH_2OH)_2$, *is a colourless viscous liquid with a sweet taste. It is used as* a solvent.

CH_2OH
|
CH_2OH (1, 2-Ethanediol)

Glycerol or Glycerine ($CH_2OH.CHOH.CH_2OH$) : A thick syrupy sweetish liquid which is soluble in water. It has the following structure

CH_2OH
|
$CHOH$ (1, 2, 3-propanetriol)
|
CH_2OH

ETHERS

General Formula — R — O — R′ where R, R′ may be alkyl or aryl group.

Functional Group —O—

Methods of Preparation :

(i) **Dehydration of alcohols**

$$2C_2H_5OH \xrightarrow[413\ K]{\text{Conc. } H_2SO_4} C_2H_5 - O - C_2H_5 + H_2O$$

(ii) **By action of diazomethane on alcohols or Phenols**

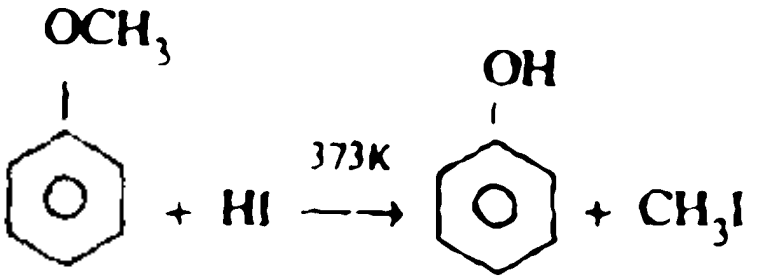
$$C_2H_5OH + CH_3N_2 \longrightarrow C_2H_5OCH_3 + N_2$$

Chemical Properties :

(i) Cleavage of C–O Bond

(a) It can be brought about by a halogen acid.

$$C_2H_5OC_2H_5 + HI \xrightarrow{373\ K} C_2H_5OH + C_2H_5I$$



(b) Cleavage with PCl_5

$$C_2H_5-O-C_2H_5 \xrightarrow{PCl_5} 2C_2H_5Cl + POCl_3$$

(c) Cleavage by H_2SO_4

$$C_2H_5-O-C_2H_5 \xrightarrow[\text{under pressure}]{\text{dil. } H_2SO_4} 2C_2H_5OH$$

$$C_2H_5-O-C_2H_5 \xrightarrow{\text{conc. } H_2SO_4}$$

$$C_2H_5OH + C_2H_5OSO_2OH$$

(ii) **Reactions of Alkyl Group :**

(a) Halogenation

$$CH_3CH_2OCH_2CH_3 \xrightarrow[\text{dark}]{Cl_2} CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HOHCH_2CH_3$$

$$\xrightarrow{Cl_2} CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HO\,\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$$

(b) Peroxide Formation

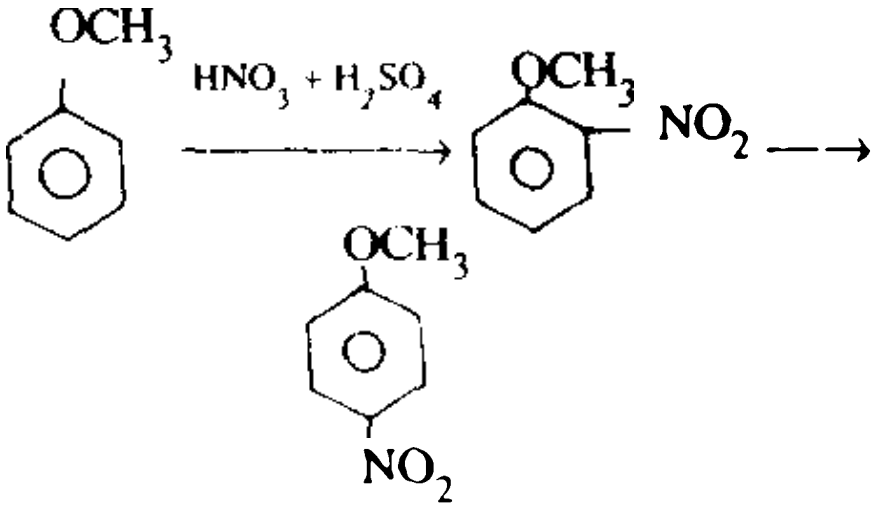
$$CH_3CH_2OCH_2CH_3 \xrightarrow[\text{light}]{O_2}$$

$$CH_3CH(OOH)\,OCH_2CH_3$$

(Unstable Peroxide, explodes on heating)

(iii) **Ring Substitution in Aromatic Ethers :**

Substitution takes place in ortho, para position



ALDEHYDES AND KETONES

Aldehydic Group $-\overset{\overset{H}{|}}{C}=O$

Ketonic Group $>C=O$

Methods of Preparation :

(i) From Acid Chlorides :

$$RCOCl + H_2 \xrightarrow[\text{Boiling xylene}]{Pd} R-\overset{\overset{O}{\|}}{C}-H + HCl$$

$$RCOCl + CdR_2 \longrightarrow RCOR' + CdCl_2$$

(ii) From Alcohols :

(a) By Catalytic Dehydrogenation

$$CH_3CH_2CH_2OH \xrightarrow[573^\circ K]{Cu} CH_3CH_2CHO + H_2$$

$$CH_3CH_3CHOH \xrightarrow[573^\circ K]{Cu} CH_3COCH_3 + H_2$$

(b) By Direct Oxidation : Aldehydes are obtained by oxidation of primary alcohols while ketones by oxidation of secondary alcohols.

$$RCH_2OH \xrightarrow[-H_2O]{[O]} RCHO$$

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!CHOH \xrightarrow[-H_2O]{[O]} \begin{matrix} R \\ R \end{matrix}\!\!>\!C = O$$

Oxidising agents are $KMnO_4/H_2SO_4$, $K_2Cr_2O_7/H_2SO_4$ air in presence of Ag as catalyst at $520^\circ K$.

(iii) From Alkynes :

$$HC \equiv CH + H_2O \xrightarrow[345\ K\ HgSO_4]{dil.\ H_2SO_4} CH_3CHO$$

$$H_3C - C \equiv CH + H_2O \xrightarrow[HgSO_4,\ 345\ K]{dil\ H_2SO_4} CH_3COCH_3$$

(iv) From Fatty acids :

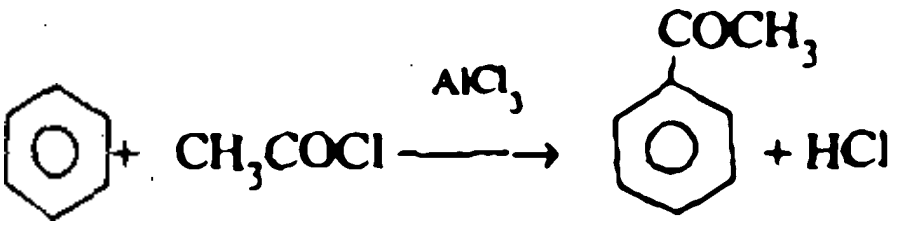
(a) By heating calcium salt of fatty acid

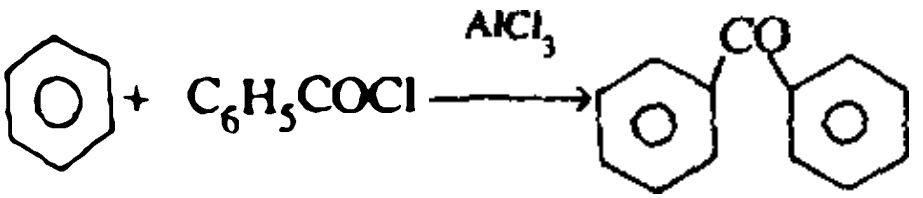
$$(CH_3COO)_2\ Ca + Ca\ (CHOO)_2 \xrightarrow{675^\circ K} 2CH_3CHO + 2CaCO_3$$

$$Ca\ (CH_3COO)_2 \xrightarrow{675^\circ K} CH_3COCH_3 + CaCO_3$$

Aromatic Aldehydes and Ketones :

(i) By Friedel Craft's Reaction—for Ketones

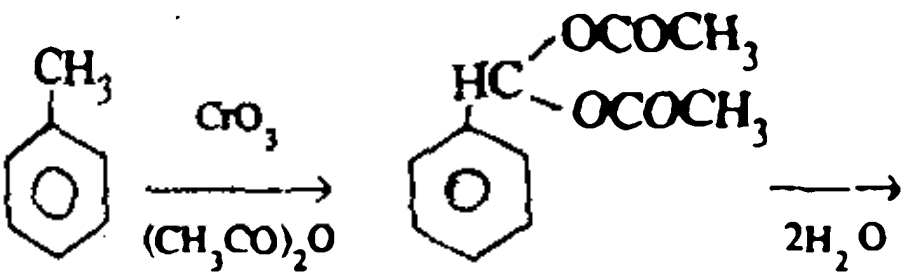


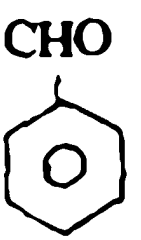


Benzophenone

+ HCl

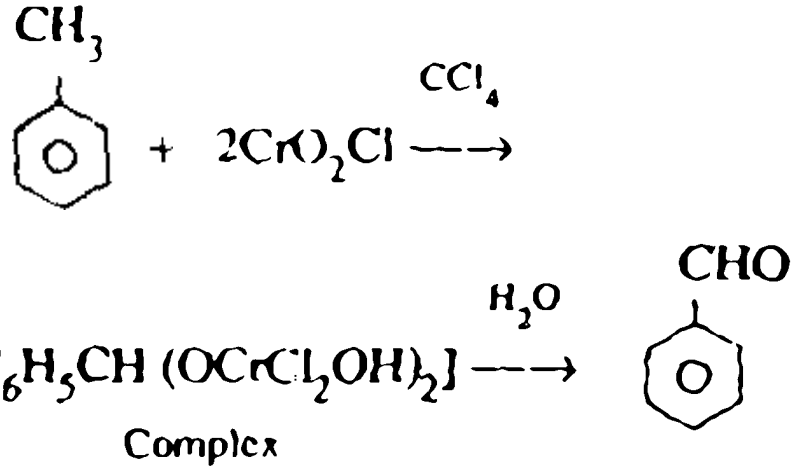
(ii) By Oxidation of Alkyl Benzenes :



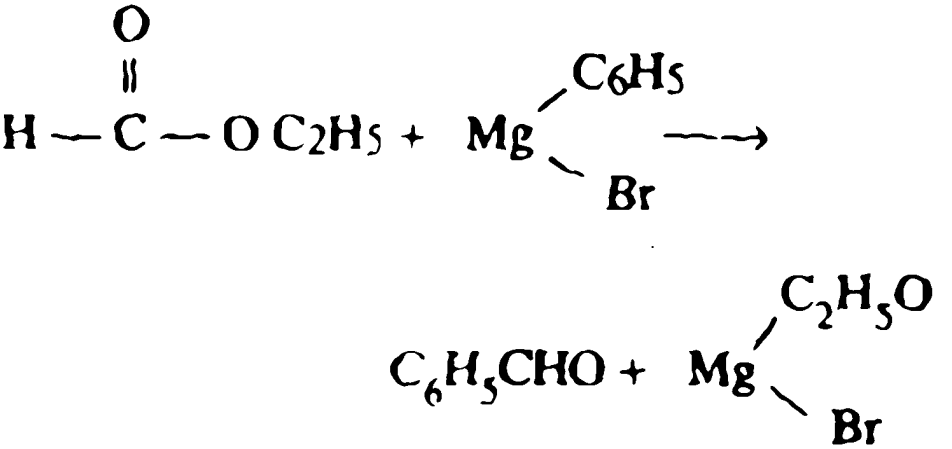


+ $2CH_3COOH$

Benzaldehyde is also prepared from toluene by Etard's Reaction.

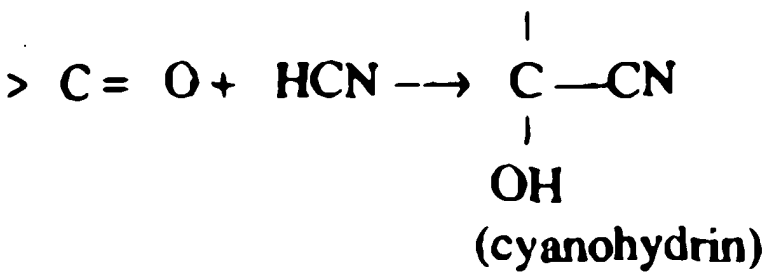


(iii) From Grignard's reagent—For Benzaldehyde



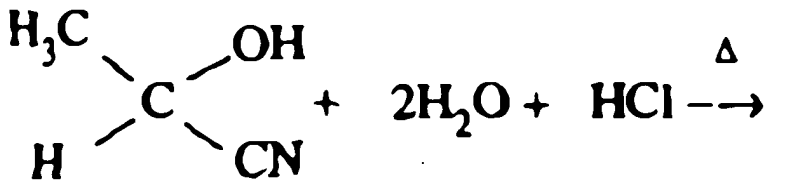
Chemical Properties :

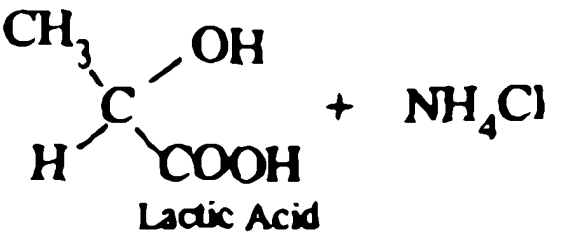
Addition Across Double Bond (C=O)



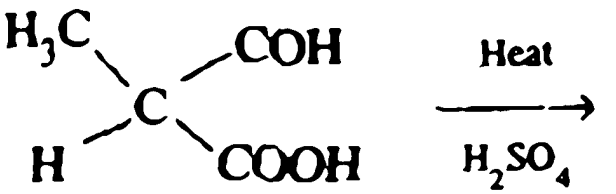
(cyanohydrin)

These cyanohydrins are used to prepare α hydroxy and α, β unsaturated acids





Lactic Acid



All aldehydes in which –CHO group is directly linked to aromatic ring dimerise on refluxing with Alc. KCN to form Benzoin.

$$C_6H_5CHO \xrightarrow[C_2H_5OH]{KCN} H_5C_6-\underset{H}{\underset{|}{C}}(OH)-\overset{O}{\overset{\|}{C}}-C_6H_5$$

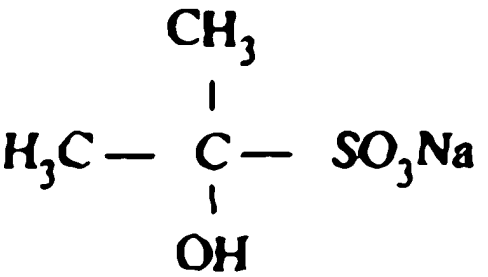
(Benzoin)

Aromatic ketones do not undergo this reaction.

Addition of Sodium bisulphite

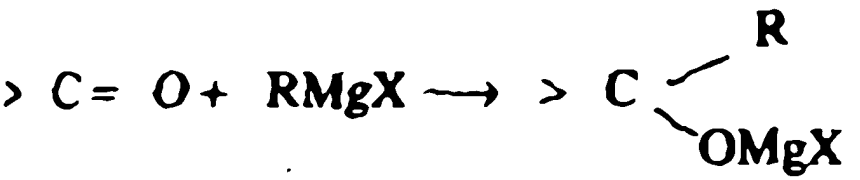
$$>C=O + NaHSO_3 \longrightarrow \underset{OH}{\underset{|}{C}}-NaSO_3^+$$

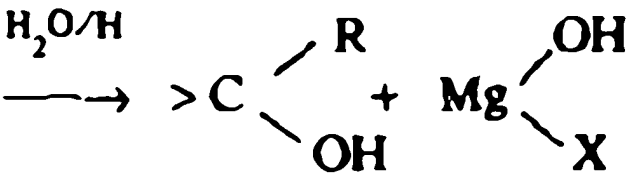
$$H_3C-\underset{CH_3}{\underset{|}{C}}=O + NaHSO_3 \longrightarrow$$



Acetone bisulphite

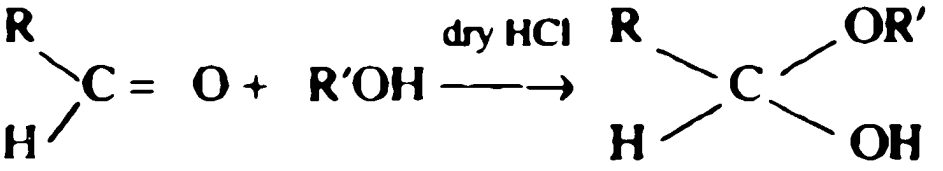
Addition of Grignard's Reagent :



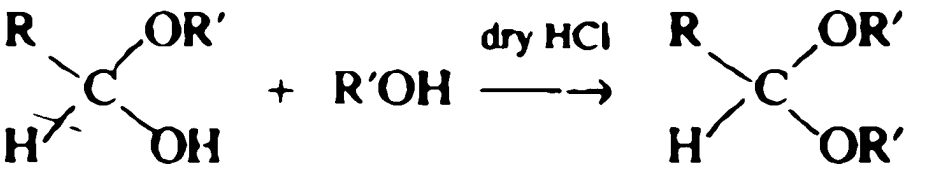


With this reaction Formaldehyde forms primary alcohols, higher aldehydes form secondary alcohols and ketones form tertiary alcohols.

Addition of Alcohols :



(Hemiacetal)



(Acetals)

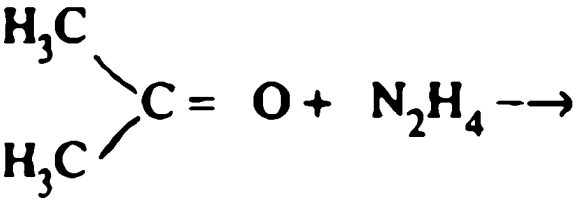
$+ H_2O$

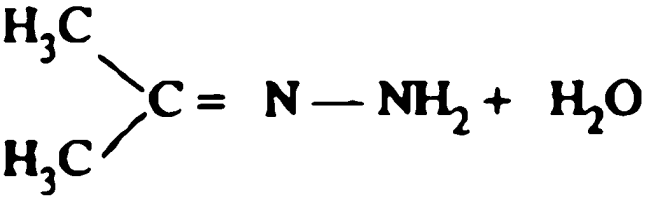
Ketones do not ordinarily react with monohydric alcohols, however they combine with diols to give cyclic ketals.

Replacement of Carnonyl Oxygen Atom with other group :

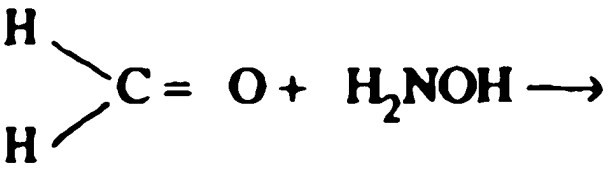
(A) Reaction with Ammonia Derivatives :

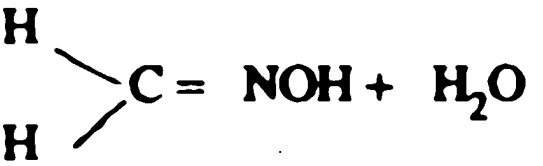
(i) Reaction with Hydrazine :



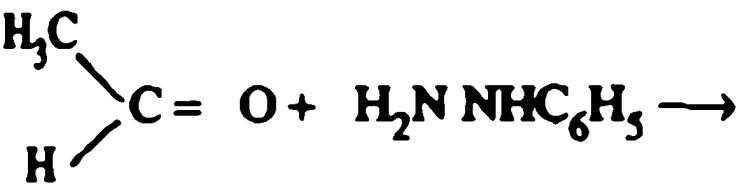


(ii) Reaction with Hydroxylamine :

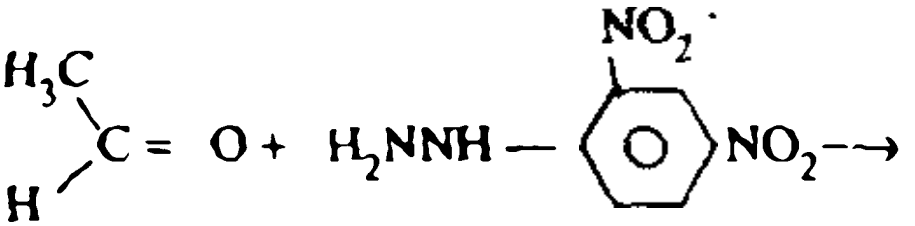


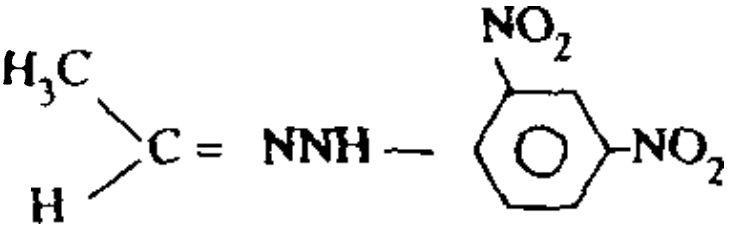


(iii) Reaction with Phenyl Hydrazine :

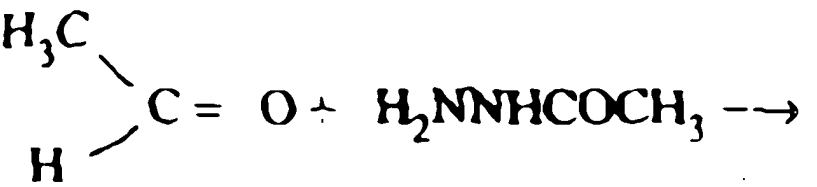


(iv) **Reaction with 2, 4-dinitrophenylhydrazine :**



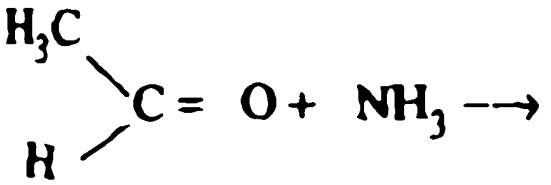


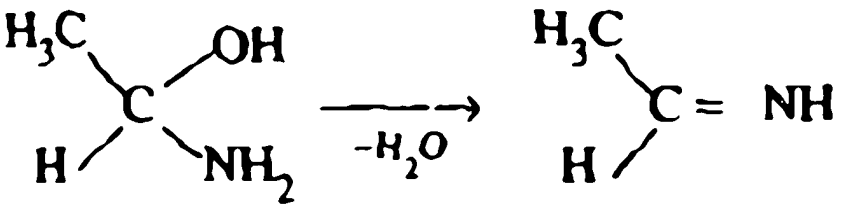
(v) **Reaction with Semi-Carbazide :**



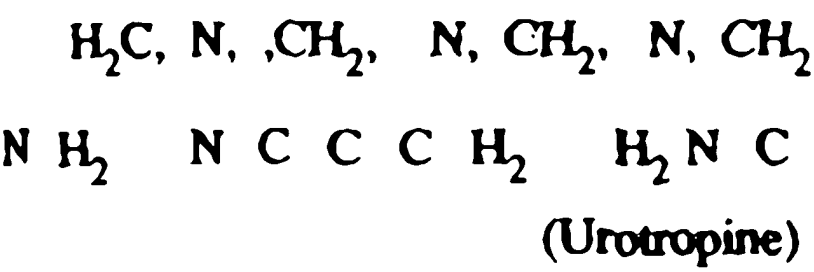
(B) Reactions with NH_3 :

Aldehydes and ketones yield imines on reaction with NH_3.





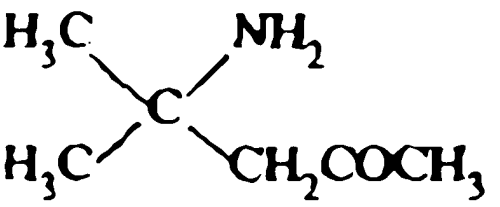
Formaldehyde reacts with ammonia to yield hexamethylene tetramine, $(CH_2)_6N_4$ which is also known as urotropine.



(Urotropine)

Acetone reacts with ammonia to yield diacetomine.

$$2\,H_3CCOCH_3 + 2\,NH_3 \longrightarrow$$



Benzaldehyde reacts with ammonia to yield hydrobenzamide.

$$3C_6H_5CHO + 2NH_3 \longrightarrow C_6H_5CH{=}N{-}CH(C_6H_5){-}CH{=}N{-}CH(C_6H_5)$$

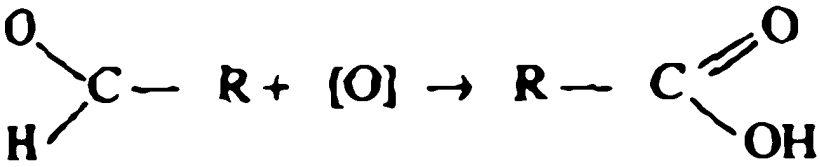
(Hydrobenzamide)

Reaction with $SOCl_2$ or PCl_5.

$$>C=O + SOCl_2 \xrightarrow{\text{Pyridine}} >CCl_2 + SO_2$$

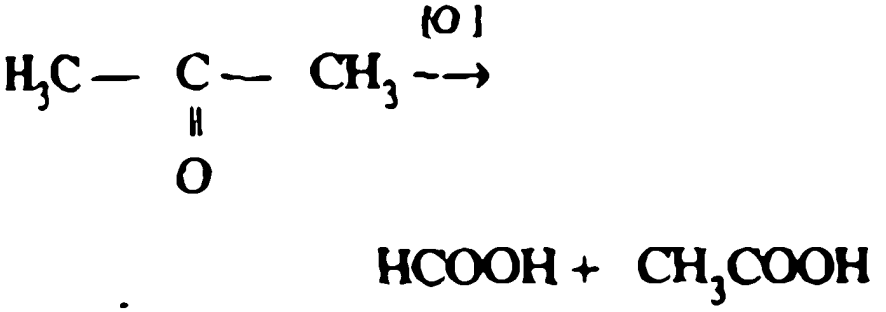
$$>C=O + PCl_5 \longrightarrow >CCl_2 + POCl_3$$

Oxidation : Aldehydes yield carboxylic acids with same number of carbon atoms.



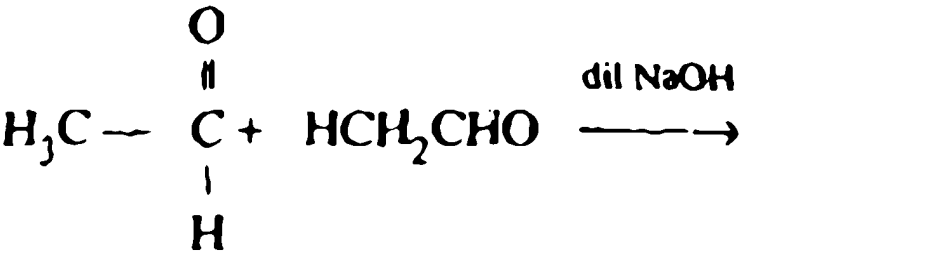
Oxidising agents used are $KMnO_4$, $K_2Cr_2O_7$ which are strong while bromine water, Ag^+, Cu^{2+} are the weak oxidising agents.

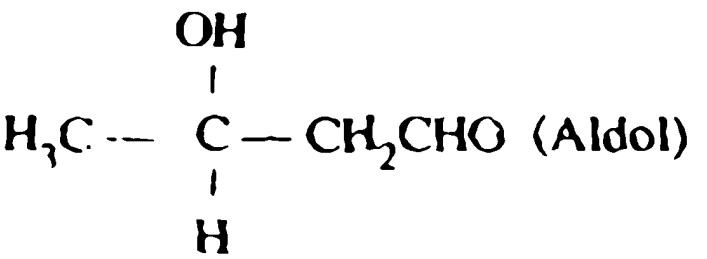
Ketones on oxidation yield a mixture of carboxylic acids by strong oxidising agents

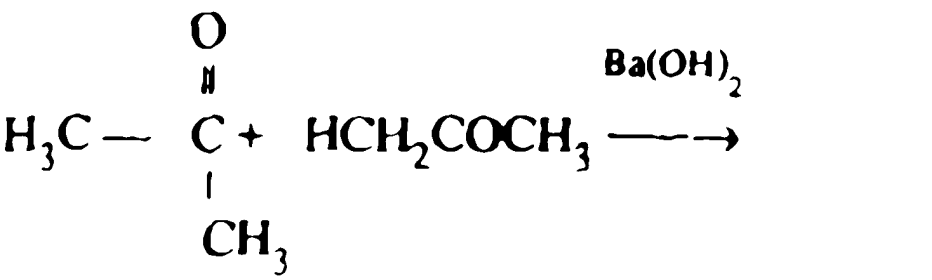


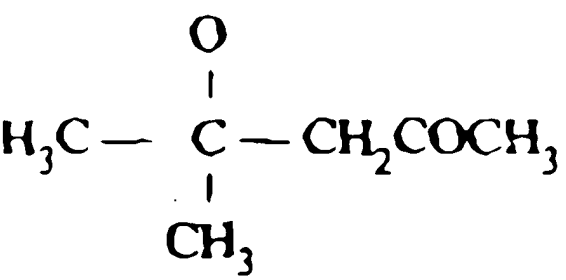
Some Important Reactions undergone by Aldehydes and Ketones :

(i) **Aldol Condensation :** Aldehydes or ketones having atleast one α-hydrogen atom condense to yield Aldol:

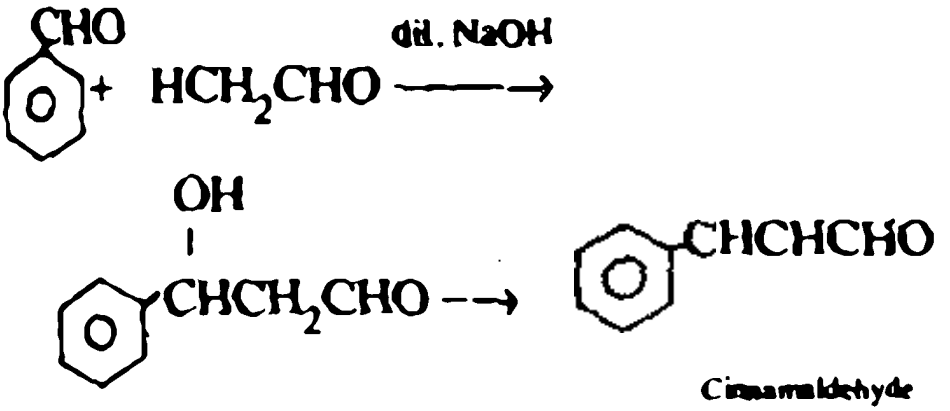




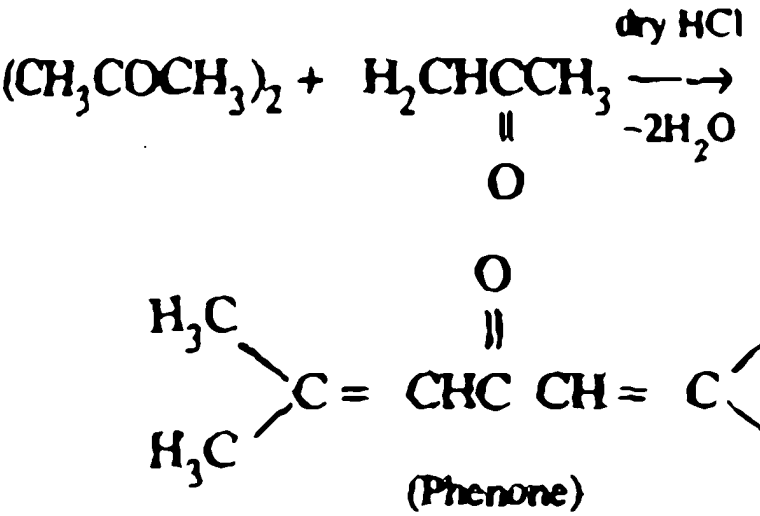




(ii) **Claisen Condensation :** It involves benzaldehyde (having no α-hydrogen) and CH_3CHO or CH_3COCH_3 (having α-hydrogen atoms)



(iii) Reaction with Acid :



(iv) Cannizzaro's Reaction : In this reaction one molecule of aldehyde is oxidised to carboxylic acid and the other is reduced to alcohol. Only those aldehydes which do not have α-hydrogen atom undergo this reaction.

$$2HCHO \xrightarrow[NaOH]{} CH_3OH + HCOONa$$

$$2C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$$

Ketones do not undergo this reaction.

CARBOXYLIC ACIDS

Functional group — $\overset{O}{\overset{\|}{C}}$ — OH

General Formula —RCOOH (R–Alkyl or Aryl radical)

Methods of Preparation :

(i) By Oxidation of Aldehydes and Ketones:

$$H_3C.CH_2CH_2 - \overset{O}{\overset{\|}{C}} - CH_3 \xrightarrow{NaOH}$$

$$CH_3CH_2CH_2COONa + CHI_3$$

$$RCHO + [O] \xrightarrow{\text{Acidic } KMnO_4} RCOOH$$

(ii) By Oxidation of Primary Alcohols :

$$RCH_2OH + 2[O] \xrightarrow{KMnO_4/H^+} RCOOH + H_2O$$

(iii) By Carboxylation of Grignard's Reagent :

$$RMgX + CO_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-OMgX \xrightarrow{H_2O/H^+} RCOOH + Mg\begin{matrix}OH\\X\end{matrix}$$

(iv) From Sodium Alkoxide and Carbon Monoxide :

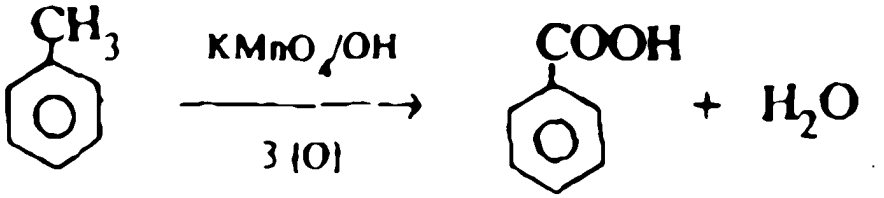
$$RONa + CO \xrightarrow[\text{pressure}]{\text{high}} RCOONa \xrightarrow{HCl}$$

$$RCOOH + NaCl$$

(v) From Alkyl Cyanides :

$$RCN + 2H_2O \xrightarrow{H^+} RCOOH + NH_4^+$$

(vi) From Alkyl Benzene :



(vii) From Olifins :

$$H_2C = CH_2 + CO + H_2O \xrightarrow[570\text{-}675\ K]{H_3PO_4} CH_3CH_2COOH$$

Chemical Properties :

(i) Reaction with alkalis

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

(ii) Reaction with Ammonia

$$RCOOH + NH_3 \longrightarrow RCOONH_4$$

(iii) Reaction with metals

$$2RCOOH + Zn \longrightarrow (RCOO)_2Zn + H_2$$

(iv) Reaction with bicarbonate and carbonate

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2 + H_2O$$

Reactions involving –OH Group removal :

(i) **Esterification**

$$RCOOH + R'OH \longrightarrow RCOOR' + H_2O$$

(ii) **Formation of Acid Anhydrides (RCO—O– OCR)**

$$RCOOH + HOOCR \longrightarrow RCOOOCR + H_2O$$

(iii) Formation of Acid Chlorides (RCOCl)

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

(iv) Formation of Acid Amides ($RCONH_2$)

$$RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$$

Reactions Involving Complete Removal of —COOH Group

(i) Soda lime decarboxylation :

$$RCOONa + NaOH \xrightarrow{CaO} RH + Na_2CO_3$$

(ii) Dry distillation of calcium salt of carboxylic acid.

(a) When calcium acetate alone is distilled acetone is formed.

(b) When calcium formate alone is distilled formaldehyde is formed.

(c) When calcium formate alongwith calcium actate is distilled acetaldehyde is formed.

(iii) **Reduction**

(a) **Partial Reduction** : Reducing agents used for the purpose are $LiAlH_4$, hydrogen in presence of copper chromite as catalyst.

$$RCOOH + H_2 \longrightarrow RCH_2OH$$

(b) **Complete Reduction** :

$$RCOOH + 6HI \xrightarrow[500^\circ K]{P} RCH_3 + 3I_2 + 2H_2O$$

(iv) **Hunsdicker Reaction** :

$$RCOOAg + Br_2 \rightarrow RBr + CO_2 + AgBr$$

Reactions Involving Alkyl Groups

(i) Oxidation

Alkyl group is oxidised at β–position. Hydrogen peroxide (H_2O_2) is used as mild oxidising agent.

$$H_3C . CH_2 . CH_2 . COOH \xrightarrow[H_2O_2]{[O]}$$

$$CH_3 . \underset{\displaystyle OH}{\underset{|}{CH}} . CH_2COOH$$

(ii) HVZ Reaction (Hell-Volhardzelinsky Reaction) : In this α-halogenation of fatty acids is carried out.

$$CH_3COOH \xrightarrow{Cl_2/P} CH_2ClCOOH \xrightarrow{Cl_2/P}$$

$$CHCl_2COOH \xrightarrow{Cl_2/P} CCl_3COOH$$

Ring Substitution Reactions in Aromatic Acids (C_6H_5COOH) :

$$C_6H_5COOH \xrightarrow{FeBr_3/Br_2} \text{(COOH, Br)} + H_2O$$

$$C_6H_5COOH \xrightarrow{HNO_3/H_2SO_4} \text{(COOH, NO}_2\text{)} + H_2O$$

$$C_6H_5COOH \xrightarrow{SO_2/H_2SO_4} \text{(COOH, -SO}_2\text{.OH)} + H_2O$$

DERIVATIVES OF CARBOXYLIC ACIDS

(A) Acyl chlorides :

General Formula $R-\overset{\overset{O}{\|}}{C}-Cl$

Methods of preparation :

(i) From Carboxylic Acids :

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

(ii) From Salts of Carboxylic Acids :

$$(CH_3COO)_2Ca + SO_2Cl_2 \longrightarrow 2CH_3COCl + CaSO_4$$

$$3CH_3COONa + PCl_3 \longrightarrow 3CH_3COCl + Na_3PO_3$$

$$2C_6H_5COONa + POCl_3 \longrightarrow 2C_6H_5COCl + NaCl + NaPO_3$$

Chemical Properties :

$R-\overset{\overset{O}{\|}}{C}-Cl$	H_2O (Hydrolysis)	RCOOH + HCl
	R'OH (Alcoholysis)	RCOOR' + HCl
	NH_3 (Ammonolysis)	$RCONH_2$ + HCl
	RCOONa	RCO –O– OCR + NaCl
	$R'NH_2$	RCONHR' + HCl *substituted amide*
	RCOOH	RCO –O– OCR + HCl

Catalytic Dehydrogenation :

$$R-\underset{\underset{O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

It is known as Rosenmund's reaction.

Reaction with $AgNO_3$:

$$RCOCl + AgNO_3 \xrightarrow{H_2O} RCOOH + AgCl + HNO_3$$

Reaction with Dialkyl Cadmium :

$$2RCOCl + R_2Cd \longrightarrow 2RCOR + CdCl_2$$

Reaction with KCN

$$RCOCl + KCN \longrightarrow KCl + RCOCN$$

Friedel Craft Reaction :

$$RCOCl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5COR + HCl$$

(B) Amides : General Formula —$RCONH_2$

$$\text{Functional Group} — \overset{\overset{O}{\|}}{C} — NH_2$$

Methods of Preparation :

(i) **From Ammonium Salts of Carboxylic Acids**

$$RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$$

(ii) **From Acid Chlorides and Acid Anhydrides**

$$RCOCl + NH_3 \longrightarrow RCONH_2 + HCl$$

$$(RCO)_2O + 2NH_3 \longrightarrow RCOONH_4 + RCONH_2$$

(iii) **From Nitriles :**

$$RCN \xrightarrow[H_2O\,/\,OH^-]{\text{Conc. HCl}} RCONH_2$$

Chemical Properties :

Amides are very feeble bases however under suitable conditions they can also show feeble acidic character. Thus they are amphoteric in nature.

$$\underset{\text{Base}}{CH_3CONH_2} + \underset{\text{Acid}}{HCl} \longrightarrow \underset{\text{Salt}}{CH_3CONH_2 \,.\, HCl}$$

$$\underset{\text{Acid}}{2CH_3CONH_2} + \underset{\text{Base}}{HgO} \longrightarrow \underset{\text{Salt}}{(CH_3CONH)_2Hg} + H_2O$$

Hydrolysis :

$$RCONH_2 + H_2O \xrightarrow{\text{dil. HCl}} RCOOH + NH_4Cl$$

Reaction with Nitrous Acid :

$$RCONH_2 + HNO_2 \longrightarrow RCOOH + N_2 + H_2O$$

Reduction :

$$RCONH_2 + 4[H] \xrightarrow[\text{or } LiAlH_4]{Na / C_2H_5OH} RCH_2NH_2 + H_2O$$

Hoffmann's Bromamide Reaction :

$$RCONH_2 + 4NaOH + Br_2 \longrightarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

Dehydration :

$$RCONH_2 \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Alkyl Nitrile}}{RCN} + H_2O$$

(C) ESTERS

General Formula $R-\overset{\overset{O}{\|}}{C}-OR'$

Functional Group $-OR'$

Methods of Preparation :

(i) Acylation :

$$R'OH + ROCl \longrightarrow R-\overset{\overset{O}{\|}}{C}-OR' + HCl$$

$$R'OH + RCOOH \xrightarrow[H_2SO_4]{} R-\overset{\overset{O}{\|}}{C}-OR' + H_2O$$

$$R'OH + RCO-O-OCR \longrightarrow R-\overset{\overset{O}{\|}}{C}-OR + RCOOH$$

(ii) By Tischenko Reaction

$$2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{H}{\overset{|}{C}}-CH_3$$

Chemical Properties :

(i) Reaction with Ammonia

$$RCOOR + NH_3 \longrightarrow RCONH_2 + ROH$$

(ii) Hydrolysis :

$$H_3CCOOC_2H_5 \xrightarrow[\text{Acid / Hydrolysis}]{H_2O / HCl} CH_3COOH + C_2H_5OH$$

$$H_3CCOOC_2H_5 \xrightarrow[\text{Basic / Hydrolysis}]{NaOH} CH_3COONa + C_2H_5OH$$

(iii) Reduction :

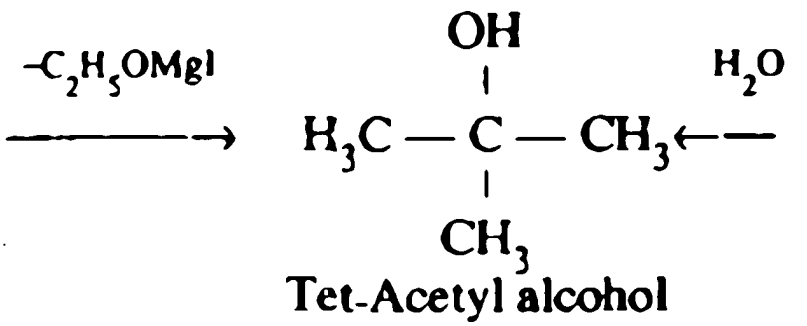
$$R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[\text{or } LiAlH_4]{Na / C_2H_5OH} RCH_2OH + ROH$$

(iv) Reaction with PCl_5 :

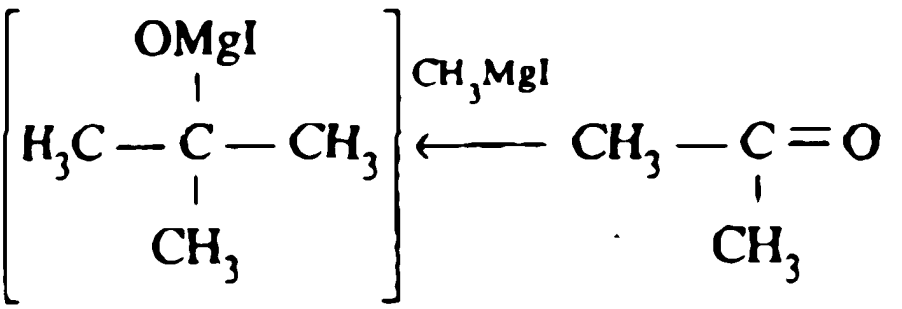
$$RCOOR' + PCl_5 \longrightarrow RCOCl + RCl + POCl_3$$

(v) Reaction with Grignard's Reagent :

$$CH_3COOC_2H_5 \xrightarrow{CH_3MgI} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgI}{|}}{C}}-OC_2H_5$$



Tet-Acetyl alcohol



acetone

(vi) Alcoholysis :

$$RCOOR' + ROH \overset{H^+}{=\!=} RCOOR + ROH$$

This is known as trans-esterification reaction.

(D) ACID ANHYDRIDES

General Formula : RCO–O–OCR

Methods of Preparation :

(i) By Reaction of Carboxylic Acid with Acid Chloride :

$$RCOOH + R'COCl \xrightarrow[\text{Pyridine}]{} RCOOOCR + HCl$$

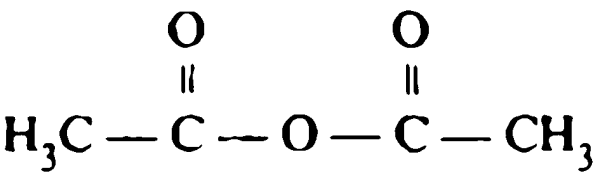
(ii) By Reaction of Acetylene with Glacial Acetic Acid :

$$C_2H_2 + 2CH_3COOH \xrightarrow{HgSO_4} H_3C - CH(OOC\,CH_3)_2$$

$$\xrightarrow[\text{Heat}]{} CH_3CHO + \begin{matrix} CH_3CO \\ \diagdown \\ \quad O \\ \diagup \\ CH_3CO \end{matrix}$$

(iii) By Passing Ketene into Glacial Acetic Acid :

$$H_2C = C = O + CH_3COOH \longrightarrow$$



(iv) By heating Carboxylic Acids with P_2O_5 :

$$RCOOH + RCOCl \xrightarrow{P_2O_5} RCOOOCR + HCl$$

Chemical Properties :

(i) Hydrolysis

$$RCOOOCR \xrightarrow[\text{Hydrolysis}]{H_2O} 2RCOOH$$

(ii) Ammonolysis

$$RCOOOCR + NH_3 \xrightarrow[\text{Ammo.}]{} RCONH_2 + RCOOH$$

(iii) $$RCOOOCR + ROH \xrightarrow[\text{Alcoholysis}]{} RCOOR + RCOOH$$

(iv) $RCOOOCR + C_6H_6 \xrightarrow{AlCl_3} C_6H_5COR + RCOOH$

(v) $RCOOOCR + PCl_5 \longrightarrow 2RCOCl + POCl_3$

(vi) $RCOOOCR + RNH_2 \longrightarrow C_6H_5COR + RCOOH$

(vii) $RCOOOCR \xrightarrow[Reduction]{LiAlH_4} RCH_2OH$

CYANIDES OR NITRILES

General formula — RCN

Functional Group – C≡N

Methods of Preparation :

(i) From Diazonium Salts :

$ArN_2X + CN^- \xrightarrow{CuCN} ArCN + N_2 + X^-$

(ii) By Dehydration of Amides :

$$RCONH_2 \xrightarrow{P_2O_5\ ,\ Heat} RCN + H_2O$$

(iii) From Alkyl Halides :

$$RX + \text{Alc. KCN} \longrightarrow RCN + KX$$

(iv) By Dehydration of Aldoximes :

$$CH_3CH = NOH \xrightarrow[-H_2O]{(CH_3CO)_2O} CH_3CN$$

(v) From Grignard's Reagent :

$$RMgX + Cl - CN \xrightarrow{\text{Ether}} RCN + Mg \begin{matrix} X \\ Cl \end{matrix}$$

Chemical Properties: (i) Hydrolysis :

(a) (Acidic)

$$RCN \xrightarrow[-HOH]{H_3O^+} RCONH_2 \xrightarrow[-HOH]{H_3O} RCOOH + NH_4^+$$

(b) (Basic)

$$RCN \xrightarrow[HOH]{OH^-} RCONH_2 \xrightarrow[HOH]{OH^-} RCOO^- + NH_3$$

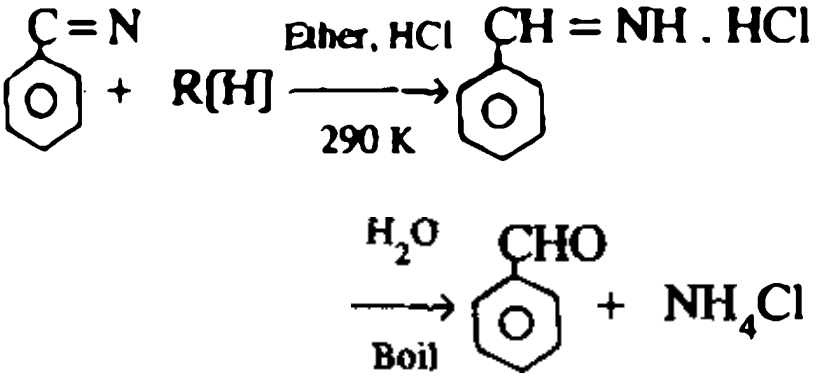
(ii) **Reduction** : On complete reduction they yield primary amines. The reducing agents used for this reaction are (a) Hydrogen in presence of Ni/Pd/Pt (b) Na / C_2H_5OH (c) $LiAlH_4$

$$RCN + 4[H] \longrightarrow RCH_2NH_2$$

On partial reduction or mild reduction using $SnCl_2$ / HCl at room temperature an imine hydrochloride is obtained which on subsequent hydrolysis with boiling water yields an aldehyde. This is called **Stephen's Reduction.**

$$H_3C.CN + 2[N] + HCl \xrightarrow[290\ k]{ether} CH_3CH = NH.HCl \xrightarrow[Boil]{H_2O} CH_3CHO + NH_4Cl$$

Similarly



(iii) Alcoholysis :

$$RCN + R'OH + H_2O \xrightarrow{H^+} R-\underset{\underset{O}{\|}}{C}-OR' + NH_4^+$$

(iv) Reaction with Grignard's Reagent :

$$RCN + R'MgX \xrightarrow{\text{ether}}$$

$$R-C(R')=NMgX \xrightarrow{H_2O/H^+} R-C(R)=O$$

CARBYLAMINES OR ISOCYANIDES OR ISONITRILES

General Formula — RNC

Functional Group — N≡C

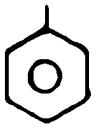
These compounds are also named as carbylamino alkanes e.g.

CH_3NC is named as carbylaminomethane and CH_3CH_2NC as carbylaminomethane.

Methods of Preparation :

(i) From Amines :

$$+ CH_3 + 3KOH \longrightarrow$$



$$+ 3KCl + 3H_2O$$

$$C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow$$

$$C_2H_5N = C + 3KCl + 3H_2O$$

This reaction is known as carbylamine reaction.

(ii) From Alkyl Halides :

$$C_2H_5Br + AgCN \xrightarrow[\text{Heat}]{C_2H_5OH} C_2H_5N = C + AgBr$$

Chemical Properties :

(i) Hydrolysis : These compounds undergo hydrolysis only in acidic medium.

$$RN = C + 2HOH \xrightarrow{H^+} RNH_2 + HCOOH$$

(ii) Reduction : They yield secondary amines when reduced with H_2 /Ni or H_2/Pt or Na / C_2H_5OH.

$$RN = C + 4[H] \longrightarrow RNH - CH_3$$

(iii) Addition Reaction :

(a) $H_3CNC + S \longrightarrow CH_3N = C = S$

Methylisocyanate

(b) $H_3CNC + Cl_2 \longrightarrow CH_3N = CCl_2$

(c) $CH_3NC + 2HgO \longrightarrow CH_3N = C = O + Hg_2O.$

NITRO COMPOUNDS

General Formula —— RNO_2 or $ArNO_2$

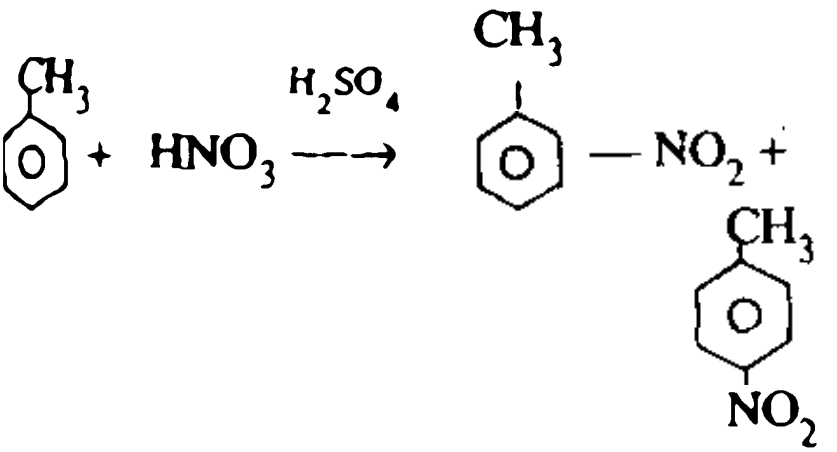
Functional Group—— $-N\begin{matrix}O\\ \\ O\end{matrix}$

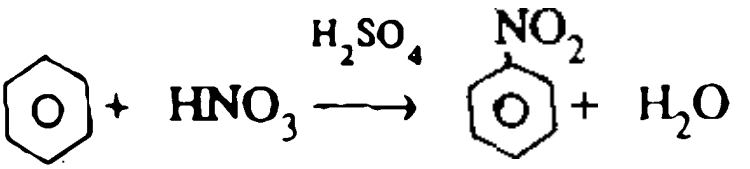
(nitroalkane)

or $-O-N=O$
(Alkyl Nitritte)

Methods of Preparation :

(i) By Direct Nitration :





(ii) From Alkyl Halides :

$$RI + Alc.AgNO_2 \longrightarrow RNO_2 + AgI$$

Chemical Properties :

(i) Hydrolysis : (a) Primary nitroalkanes when hydrolysed with conc. HCl or 85% H_2SO_4 yield acids and hydroxylamine.

(b) Secondary nitroalkanes on hydrolysis with boiling HCl give ketone and nitrous oxide.

$$2R_2CHNO_2 \longrightarrow 2R_2C=O + N_2O + H_2O$$

(c) Tertiary nitro compounds do not hydrolyse with boiling HCl.

(ii) Action with Nitrous Acid :

(a) $RCH_2NO_2 + HNO_2 \longrightarrow$

$$R-\underset{\displaystyle NO_2}{\underset{|}{C}}=N-OH + H_2O$$

Nitrolic Acid

(b) $R_2CHNO_2 + HNO_2 \longrightarrow$

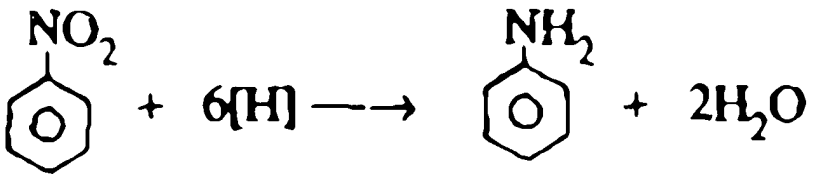
$$R-\underset{\displaystyle NO_2}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}}-N=O + H_2O$$

Pseudo nitrole

(c) Tertiary nitroalkanes do not react with HNO_2.

(iii) **Reduction :** (a) On reduction with H_2 / Ni, H_2 / Pt, Sn / HCl, $LiAlH_4$ or Fe / HCl, the nitro group yields primary-amino group.

$$RNO_2 + 6[H] \longrightarrow RNH_2 + 2H_2O$$

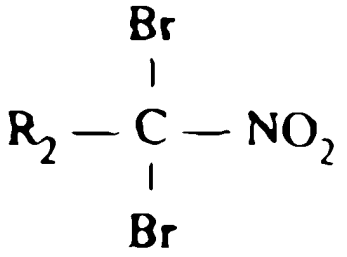


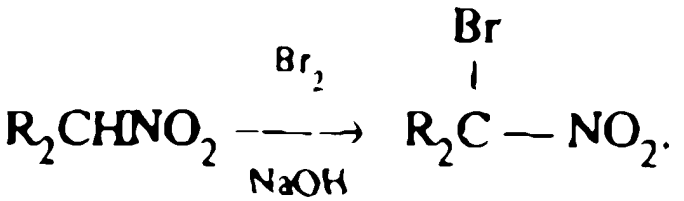
(b) On reduction with Zn /NH_4Cl, $-NO_2$ *yields* –NHOH.

$$CH_3NO_2 + 4[H] \xrightarrow{Zn\,/\,NH_4Cl} \underset{\text{Hydroxylamine}}{CH_3NHOH} + H_2O$$

(iv) **Halogenation :**

$$RCH_2NO_2 \xrightarrow[NaOH]{Br_2} R-\underset{\displaystyle Br}{\underset{|}{C}}HNO_2 \xrightarrow[NaOH]{Br_2}$$





AMINES

General Formula

Primary Amine ——— RNH_2

Secondary Amine —— R_2NH

Tertiary Amine ——— R_3N

Functional Group

Primary Amine $-NH_2$

Secondary Amine $-\underset{|}{NH}$

Tertiary Amine $-\underset{|}{N}-$

Methods of Prepartion :

(a) By Reduction of Amides :

$$RCONH_2 \xrightarrow[\text{or } LiAH_4]{Na / C_2H_5OH} RCH_2NH_2 + H_2O$$

(b) By Reduction of Oximes :

$$RCH = NHOH \xrightarrow[\text{or } LiAlH_4]{Na / C_2H_5OH} RCH_2NH_2 + H_2O$$

(c) From Alkyl Halides (By Ammonolysis)

$$RX + 2NH_3 \longrightarrow RNH_2 + NH_4X$$

$$RNH_2 + RX \longrightarrow R_2NH + HX$$

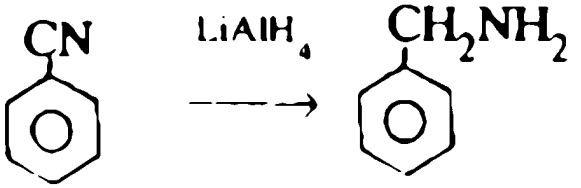
$$R_2NH + RX \longrightarrow R_3N + HX$$

$$R_3N + RX \longrightarrow R_4N^+X^-$$

(d) By Reduction of Alkyl Cyamindes (Menduis Reaction) :

On reduction with H_2 / Ni, $LiAlH_4$, Na / C_2H_5OH.

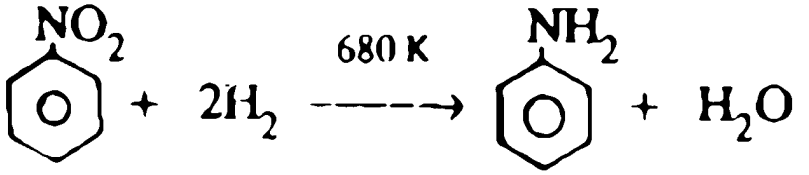
$$RCN + 4[H] \longrightarrow RCH_2NH_2$$



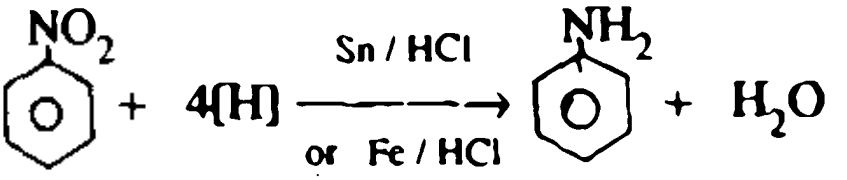
(e) By Hoffmann's Bromamide Reaction :

$$RCONH_2 + Br_2 + 4KOH \xrightarrow{343\ K} RNH_2 + 2KBr + K_2CO_3 + 2H_2O$$

(f) From Nitrobenzene :



$$+ 2H_2 \longrightarrow + H_2O$$



(g) From Alcohols :

$$ROH + NH_3 \xrightarrow[-H_2O]{Al_2O_3,\ 575\ K} RNH_2$$

$$\xrightarrow[-H_2O]{+ROH} R_2NH \xrightarrow[H_2O]{+ROH} R_3N$$

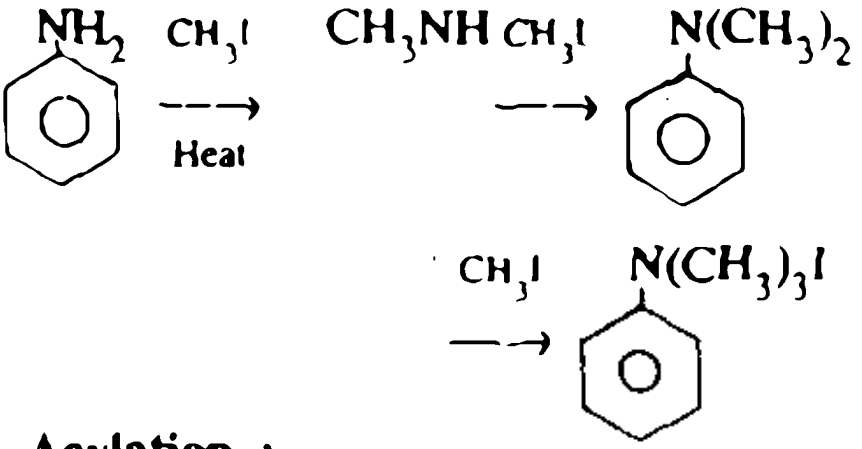
Chemical Properties :

Alkylamines are stronger bases than ammonia. Aniline ($C_5H_5NH_2$) is a weaker base than ammonia.

(i) Alkylation

$$RNH_2 + RX \longrightarrow R_2NH \xrightarrow{RX} R_3N$$

$$\xrightarrow{RX} R_4N^+X^-$$

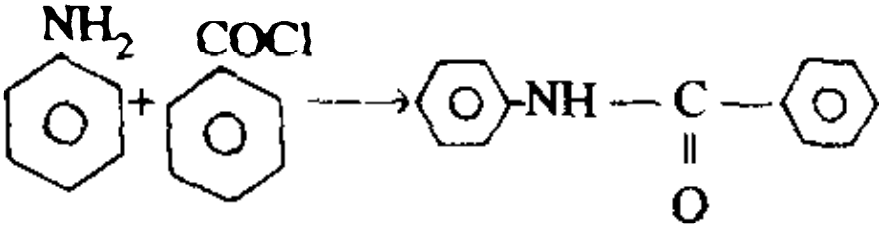


(ii) Acylation :

$$C_2H_5NH_2 + CH_3COCl \longrightarrow C_2H_5NHCOCH_3 + HCl$$

$$C_6H_5NH_2 + CH_3COCl \longrightarrow C_6H_5NHCOCH_3 + HCl$$

The reaction of aniline with acid chloride of aromatic acid is known as **Schotten Boumann** Reaction e.g.



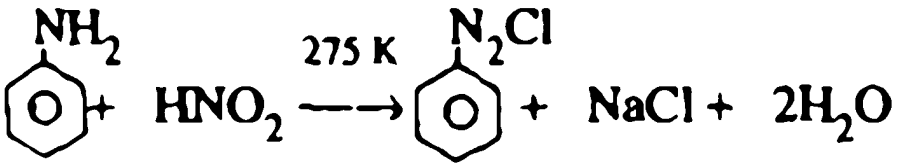
Benzanilide

(iii) Reaction with Metal Ions :

$$2C_2H_5NH_2 + AgCl \longrightarrow \left[(C_2H_5NH_2)_2Ag\right]^+ Cl^-$$

$$4\,C_2H_5NH_2 + CuSO_4 \longrightarrow \left[(C_2H_5NH_2)_4Cu\right]^{2+} SO_4^{2-}$$

(iv) Reactions with Nitrous Acid :



This reaction with primary amine is known as diazotisation.

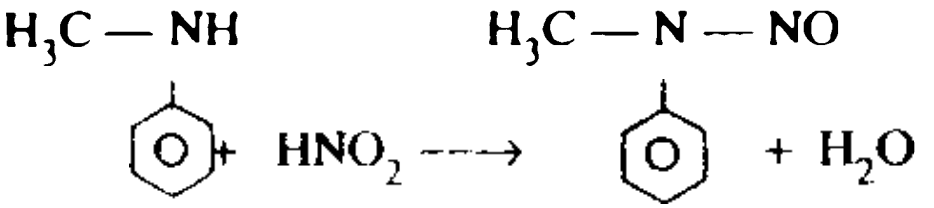
Primary Aliphatic Amine :

$$C_2H_5NH_2 + HNO_2 \longrightarrow [C_2H_5N_2^+Cl^-]$$

$$\xrightarrow{H_2O} C_2H_5OH$$

$$\longrightarrow CH_2 = CH_2 + N_2 + HCl$$

Secondary Aliphatic and Aromatic Amines :



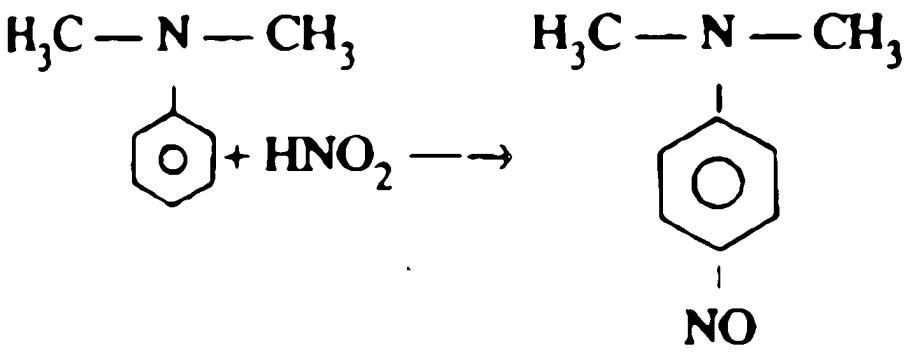
N – nitroso
N – Methyl aniline

$$(C_2H_5)_2NH + HNO_2 \longrightarrow$$

$$(C_2H_5)_2N - NO + H_2O$$

Tertiary aliphatic amine when warmed with nitrous acid yield nitrites while tertiary aromatic amines undergo electrophilic substitution at the ring.

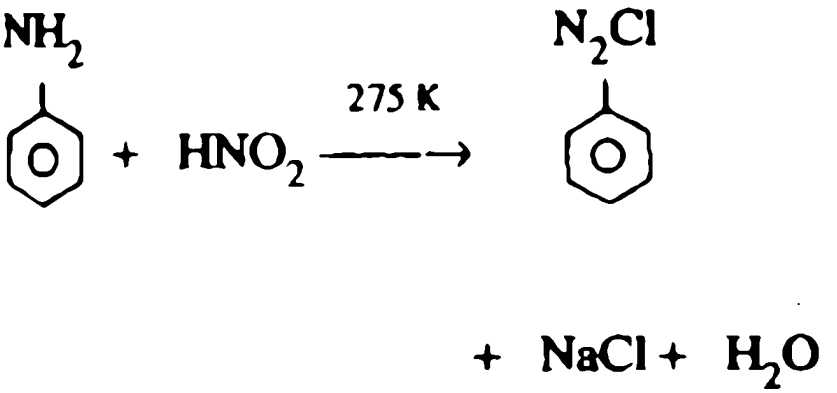
$$(C_2H_5)_3N + HNO_2 \longrightarrow \left[(C_2H_5)_3NH\right]^{+} NO_2^{-}$$



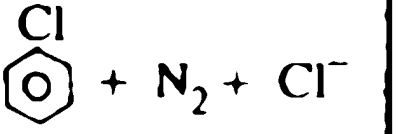
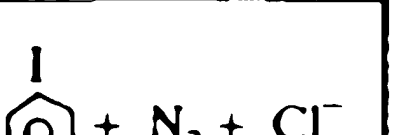
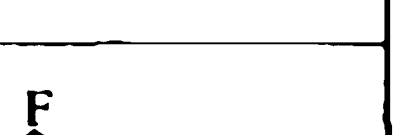
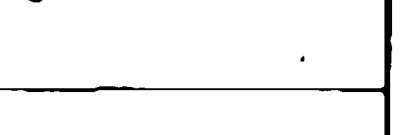
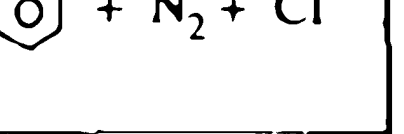
Ring Substitution Reaction in Aniline

Electrophilic substitution occurs in benzene ring in ortho-, para- positions during nitration, halogenation, acylation etc.

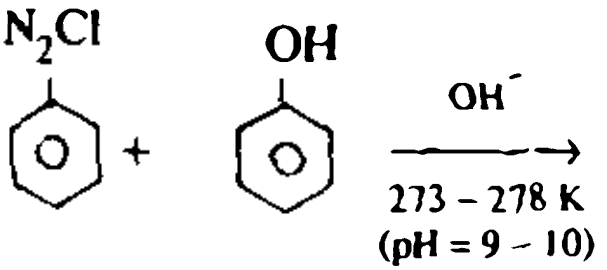
Formation of Diazonium Salt : Primary aromatic amines form such salts.

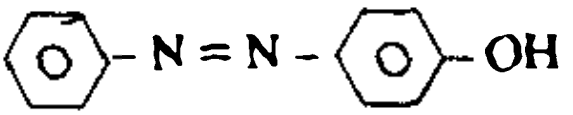


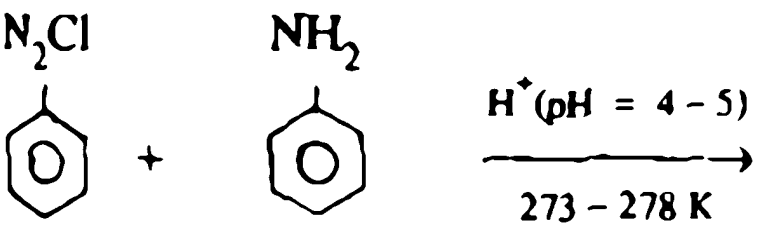
Diazonium salts can undergo a large number of replacement reactions.

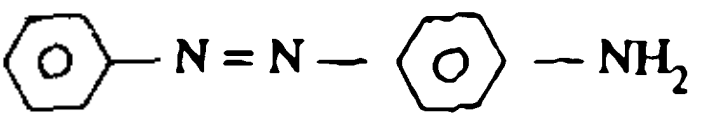
$C_6H_5N_2Cl$	CuCl	
	KI	
	HBF_4 Heat	
	dil. H_2SO_4 warm	
	H_3PO_2	

Diazonium salts can also undergo coupling reactions.


N2Cl
OH
OH⁻
273 – 278 K
(pH = 9 – 10)


N = N
OH


N2Cl
NH2
H⁺(pH = 4 – 5)
273 – 278 K


N = N
NH2

ANALYTICAL CHEMISTRY

QUALITATIVE INORGANIC ANALYSIS

In qualitative analysis the given mixture is analysed for acidic and basic radicals i.e. for anions and cations that it contains.

Depending upon the quantity of sample made available it is classified as :

Macro Analysis . . . 0.1–1 g

Semi-micro Analysis . . . 10–100 mg

Micro analysis . . . 1–10 mg

The common procedure for testing an unknown sample is to make its solution and then test this solution for different ions present. Steps involved in the systematic analysis of a given sample are (A) Preliminary Tests :

(i) Colour and smell

(ii) Flame Test

(iii) Borax Bead Test

(b) Tests for Acid Radicals (Anions)

(i) dil. acid test (dil. H_2SO_4)

(ii) Conc. acid test (conc. H_2SO_4)

(iii) Wet tests for acid radicals

(C) Wet Tests for Basic Radicals

(a) Preliminary Tests

(i) Colour and smell

Colour	*Ion Indicated*
Blue/Bluish Green	Cu^{2+} or Ni^{2+}
Greenish	Ni^{2+}
Light Green	Fe^{2+}
Dark Green	Cr^{3+}
Pink	Co^{2+}

Colour	*Ion Indicated*
Light Pink, Flesh colour or earthy colour	Mn^{2+}
Dark Brown	Fe^{3+}

Smell	*Ion Indicated*
Ammonical smell	NH_4^+
Vinegar like smell	CH_3COO^-
Smell of rotten egg	S^{2-}

(ii) Flame Test

Colour of Flame	*Ion Indicated*
Brick Red	Ca^{++}
Crimson Red	Sr^{++}
Grassy Green	Ba^{++}
Bright-Bluish Green	Cu^{++}

(iii) Borax Bead Test

Colour of bead in oxidising flame	*Ion Indicated*
Green in hot, light brown in cold	Copper (Cu^{++})
Pinkish violet in both hot and cold	Manganese (Mn)

Colour of bead in oxidising flame	*Ion Indicated*
Yellowish brown in hot and pale yellow in cold	Iron (Fe^{+++})
Brown in hot and pale brown in cold	Nickel (Ni^{++})

(B) (i) Dilute Sulphuric Acid Test

Gas evolved	*Ion Indicated*
Colourless, odourless gas which turns water milky (CO_2)	CO_3^{2-}
Colourless, pungent smell, which turns acidified potassium dichromate paper green (SO_3)	SO_3^{--}

Colourless, smell like that of rotten eggs, turns lead acetate paper black (H_2S)	S^{2-}
Reddish brown in colour, pungent smell, turns ferrous sulphate solution black (NO_2)	NO_2^-

(ii) Concentrated Sulphuric Acid Test

Gas evolved	*Ion Indicated*
Colourless gas with pungent smell, white fumes with NH_4OH, white ppt. with $AgNO_3$ solution (HCl)	Cl^-
Reddish brown vapours with pungent smell, turns starch paper yellow but does not turn $FeSO_4$ solution black (Br_2)	Br^-

Deep violet vapours with pungent smell, turns starch paper blue	I^-
Reddish brown gas with pungent smell, turns $FeSO_4$ solution black (NO_2)	NO_3^-
Colourless vapours, vinegar smell, turns blue litmus red (CH_3COOH)	CH_3COO^-

(iii) Wet Tests for Acid Radicals :

(a) Carbonate (CO_3^{2-}) :

Reaction with dilute HCl.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

CO_2 gas when passed in lime water

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

(b) Sulphide (S^{2-}) :

Lead Acetate Test :

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{Black ppt.}}{PbS\downarrow} + 2CH_3COONa$$

Sodium Nitroprusside Test :

$$Na_2S + \underset{\text{Sodium Nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Violet or Purple Colour}}{Na_4[Fe(CN)_5NOS]}$$

Cadmium Carbonate Test :

$$Na_2S + CdCO_3 \longrightarrow \underset{\text{Yellow ppt.}}{CdS} + Na_2CO_3$$

(c) Sulphite (SO_3^{2-}) :

Potassium Dichromate Test

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$Na_2SO_3 + O \longrightarrow Na_2SO_4$$

Barium Chloride Test :

$$Na_2SO_3 + BaCl_2 \longrightarrow BaSO_3 \downarrow + 2NaCl$$

white ppt.

$$BaSO_3 + 2HCl \longrightarrow BaCl_2 + SO_2 + H_2O$$

Potassium Permanganate Test :

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$Na_2SO_3 + O \longrightarrow Na_2SO_4$$

(d) Nitrite (NO_2^-) :

Potassium Iodide Test :

$$2KI + 2H_2SO_4 + 2HNO_2 \longrightarrow 2KHSO_4 + 2NO + I_2 \uparrow + 2H_2O$$

Liberated iodine turns starch paper blue.

Ferrous Sulphate Test :

$$CH_3COOH + KNO_2 \longrightarrow CH_3COOK + HNO_2$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

$$FeSO_4 + NO \longrightarrow \underset{\text{Dark Brown}}{FeSO_4 . NO}$$

(e) Chloride (Cl^-) :

MnO_2 Test :

$$2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2 \uparrow$$

$AgNO_3$ Test :

$$KCl + AgNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCl} + KNO_3$$

$$AgCl + 2NH_4OH \longrightarrow$$

$$[Ag(NH_3)_2]Cl + 2H_2O$$

Soluble Complex

Chromyl Chloride Test :

$$4KCl + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow$$

$$3K_2SO_4 + 2CrO_2Cl_2 + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4$$

Chromyl Chloride — Sod. Chromate

$$+ 2H_2O + 2NaCl$$

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow PbCrO_4 +$$

Lead chromate yellow ppt.

$$2CH_3COONa$$

(f) Bromide (Br^-) :

MnO_2 Test :

$$2KBr + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 +$$

$$MnSO_4 + 2H_2O + Br_2$$

$AgNO_3$ Test :

$$KBr + AgNO_3 \longrightarrow \underset{\text{Pale yellow ppt.}}{AgBr\downarrow} + KNO_3$$

Pale yellow ppt. of silver bromide is sparingly soluble in NH_4OH.

Chlorine water test :

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$

Bromine being soluble in CCl_4 imparts an orange colour to the layer.

(g) Iodide (I^-) :

MnO_2 Test :

$$2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2$$

$AgNO_3$ Test :

$$KI + AgNO_3 \longrightarrow KNO_3 + \underset{\text{yellow ppt.}}{AgI}$$

Chlorine Water Test :

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

Iodine being soluble in CCl_4 imparts a violet colour to the CCl_4 layer.

(h) Nitrate (NO_3^-) :

Ring Test :

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow$$

$$3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

$$FeSO_4 + NO + 5H_2O \longrightarrow [Fe(NO)(H_2O)_5]SO_4$$

Brown Ring

Copper Test :

$$2NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_3$$

$$4HNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Reddish brown

(i) Acetate (CH_3COO^-) :

Oxalic Acid Test :

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} + 2CH_3COONa \longrightarrow \begin{array}{l} COONa \\ | \\ COONa \end{array} + 2CH_3COOH$$

Vinegar smell

Ferric Chloride Test :

$$3CH_3COONa + FeCl_3 \longrightarrow (CH_3COO)_3Fe + 3NaCl$$

$$(CH_3COO)_3Fe + 2H_2O \longrightarrow (CH_3COO)(OH)_2Fe + 2CH_3COOH$$

(j) Sulphate (SO_4^{2-}) :

Barium Chloride Test :

$$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2NaCl$$

White ppt.

Lead Acetate Test :

$$Na_2SO_4 + Pb(CH_3COO)_2 \longrightarrow$$

$$PbSO_4 + 2CH_3COONa$$

(k) Phosphate (PO_4^{3-}) :

Ammonium Molybdate Test :

$$K_3PO_4 + 3(NH_4)_2MoO_4 \longrightarrow$$

Amm. Molybdate

$$2(NH_4)_3PO_4 + 3K_2MoO_4$$

$$K_2MoO_4 + 2HNO_3 \rightarrow H_2MoO_4 + 2KNO_3$$

Molybdate acid

$$H_2MoO_4 \longrightarrow MoO_3 + H_2O$$

$$(NH_4)_3PO_4 + 12MoO_3 + 6H_2O \longrightarrow$$

$$(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 6H_2O$$

Amm. Phospho molybdate
(Yellow ppt.)

Magnesia Mixture Test :

$$Na_2HPO_4 + MgCl_2 + NH_4OH \longrightarrow$$

Disodium Hydrogen Phosphate

$$Mg(NH_4)PO_4 + 2NaCl + H_2O$$

Mag. Amm. Phosphate (white ppt.)

Classification of Basic Radicals (Cations) into Group

Group	*Group Reagent*	*Cations*	*Form of ppt.*
I (silver group)	Dilute HCl	Pb^{2+}	Chlorides
II (copper group)	H_2S in presence of dilute HCl	Pb^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+} etc.	Sulphides

Group	*Group Reagent*	*Cations*	*Form of ppt.*
III (Iron group)	NH_4OH in presence of NH_4Cl	Ag^+, Fe^{3+}, Al^{3+}	Hydroxides
IV (Zinc group)	H_2S in presence of NH_4OH	Ni^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}	Sulphides
V (Calcium group)	$(NH_4)_2CO_3$ in presence of NH_4OH	Ca^{2+}, Ba^{2+}, Sr^{2+}	Carbonates
VI (Alkali group)		NH_4^+, Mg^{2+}	

Reactions Involved in Group I Analysis :

$$Pb(NO_3)_2 + 2HCl \longrightarrow \underset{\text{White ppt.}}{PbCl_2} + 2HNO_3$$

Confirmatory Tests :

(i) On cooling, the precipitate settles down as $PbCl_2$ is less soluble in cold water.

(ii) Potassium chromate test

$$\underset{\text{Hot solution}}{PbCl_2} + K_2CrO_4 \longrightarrow \underset{\text{Yellow ppt.}}{PbCrO_4} + 2KCl$$

(iii) Potassium Iodide test

$$\underset{\text{Hot solution.}}{PbCl_2} + 2KI \longrightarrow \underset{\text{Yellow ppt.}}{PbI_2} + 2KCl$$

Reactions Involved in Group II Analysis : Passing of H_2S gas through the acidified original solution will provide the precipitate of radicals Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+} and As^{3+} as their sulphides.

$$HgCl_2 + H_2S \longrightarrow \underset{\text{Black ppt.}}{HgS\downarrow} + 2HCl$$

$$PbCl_2 + H_2S \longrightarrow \underset{\text{Black ppt.}}{PbS\downarrow} + 2HCl$$

$$CuCl_2 + H_2S \longrightarrow \underset{\text{Black ppt.}}{CuS\downarrow} + 2HCl$$

$$CdCl_2 + H_2S \longrightarrow \underset{\text{Yellow ppt.}}{CdS\downarrow} + 2HCl$$

$$2AsCl_3 + 3H_2S \longrightarrow \underset{\text{Yellow ppt.}}{As_2S_3\downarrow} + 6HCl$$

Sulphides of Group IIA (copper group) are insoluble in yellow ammonium sulphide while that of IIB (Arsenic groups) are soluble. By treating with yellow ammonium sulphide groups IIA and IIB are separated.

$$As_2S_3 + 3(NH_4)_2S + 2S \longrightarrow \underset{\text{Amm. Thioarsenate}}{2(NH_4)_3AsS_4\ (\text{soluble})}$$

Confirmatory Test for Arsenic :

$$As_2S_3 + 10HNO_3 \longrightarrow \underset{\text{Soluble}}{2H_3AsO_4} + 10NO_2 + 3S + 2H_2O$$

(i) Ammonium Molybdate Test :

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow$$

$$(NH_4)_3AsO_4 . 12MoO_3\downarrow + 21NH_4NO_3 + 12H_2O$$

Yellow ppt.

(ii) Magnesia Mixture Test :

$$H_3AsO_4 + MgSO_4 + 3NH_4OH \longrightarrow$$

$$Mg(NH_4)AsO_4 + (NH_4)_2SO_4 + 3H_2O$$

White ppt.

Mercury (Hg^{2+}) : Black HgS is ir. soluble in 50% nitric acid. It dissolves in aqua-regia forming $HgCl_2$.

$$3HgS + 2HNO_3 + 6HCl \longrightarrow 3HgCl_2 + 2NO + 4H_2O + 3S$$

(i) Potassium Iodide Test :

$$HgCl_2 + 2KI \longrightarrow HgI_2 + 2KCl$$

Red ppt.

$$HgI_2 + 2KI \longrightarrow \underset{\text{Soluble}}{K_2[HgI_4]}$$

(ii) Copper Chips Test

$$HgCl_2 + Cu \longrightarrow CuCl_2 + \underset{\text{White deposit}}{Hg}$$

(iii) Stannous Chloride Test :

$$2HgCl_2 + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{White}}{Hg_2Cl_2}$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{Grey}}{2Hg}$$

Lead (Pb^{2+}) : Black ppt. of PbS dissolves in 50% nitric acid. On adding H_2SO_4, lead sulphate is precipitated.

$$3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 4H_2O + 2NO + 3S$$

$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow \underset{\text{White}}{PbSO_4\downarrow} + 2HNO_3$$

(i) KI Test :

$$Pb(NO_3)_2 + 2KI \longrightarrow 2KNO_3 + \underset{\text{Yellow}}{PbI_2\downarrow}$$

(ii) K_2CrO_4 Test :

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow 2KNO_3 + \underset{\text{(yellow)}}{PbCrO_4}$$

Copper (Cu^{2+}) : Black ppt. of CuS dissolves in 50% nitric acid and blue solution is obtained on addition of excess of NH_4OH

$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O + 3S$$

$$Cu(NO_3)_2 + 4NH_4OH \rightarrow \underset{\text{Blue solution.}}{[Cu(NH_3)_4](NO_3)_2} + 4H_2O$$

(i) Potassium Ferrocyanide Test :

$$[Cu(NH_3)_4]SO_4 + 4CH_3COOH \longrightarrow$$

$$CuSO_4 + 4CH_3COONH_4$$

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow$$

$$Cu_2[Fe(CN)_6] + 2K_2SO_4$$

(Choclate brown) colour

(ii) Potassium Iodide Test

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + I_2 + 2K_2SO_4$$

White ppt.

Cadmium (Cd^{2+}) : The yellow ppt. is dissolved in 50% nitric acid

$$3CdS + 8HNO_3 \longrightarrow 3Cd(NO_3)_2$$

$$+ 4H_2O + 2NO + 3S$$

(i) Sodium Hydroxide Test :

$$Cd(NO_3)_2 + 2NaOH \rightarrow Cd(OH)_2 + 2NaNO_3$$

White ppt.

(ii) Potassium Ferrocyanide Test :

$$2Cd(NO_3)_2 + K_4[Fe(CN)_6] \rightarrow \underset{\text{White ppt}}{Cd_2[Fe(CN)_6]} + 4KNO_3$$

Reactions involved in Group III Analysis

$$FeCl_3 + 3NH_4OH \rightarrow \underset{\text{Reddish brown}}{Fe(OH)_3\downarrow} + 3NH_4Cl$$

$$AlCl_3 + 3NH_4OH \rightarrow \underset{\text{(White)}}{Al(OH)_3\downarrow} + 3NH_4Cl$$

Iron (Fe^{3+}) : The reddish brown ppt. of $Fe(OH)_3$ is dissolved in HCl.

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

i) Potassium Ferrocyanide Test :

$$FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\substack{\text{Ferric ferrocyanide}\\ \text{(Prussian Blue)}}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

(ii) Potassium Sulphocyanide Test :

$$FeCl_3 + 3KCNS \longrightarrow Fe(CNS)_3 + 3KCl$$

Ferric Sulphocyanide
(Blood Red)

Aluminium (Al^{3+}) :

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

(dissolution)

$$AlCl_3 + 3NH_4OH \rightarrow 3NH_4Cl + Al(OH)_3 \downarrow$$

Reaction Involved in Group IV Analysis

Cobalt (Co^{2+}) :

(i) Potassium Nitrite Test :

$$CoCl_2 + 2KNO_2^- \longrightarrow Co(NO_2)_2 + 2KCl$$

$$KNO_2 + CH_3COOH \rightarrow CH_3COOK + HNO_2$$

$$Co(NO_2)_2 + 2HNO_2 \longrightarrow Co(NO_2)_3$$

Cobaltic Nitrite

$$+ H_2O + NO$$

$$Co(NO_2)_3 + 3KNO_2 \longrightarrow K_3[Co(NO_2)_6]$$

Yellow ppt.

(ii) Ammonium Thiocyanate Ether Test

$$CoCl_2 + 4NH_4CNS \dashrightarrow$$

$$(NH_4)_2[Co(CNS)_4] + 2NH_4Cl$$

Nickel (Ni^{2+}) :

(i) Sodium Hydroxide-Bromine Water Test :

$$NiCl_2 + 2NaOH \dashrightarrow Ni(OH)_2 + 2NaCl$$

Green ppt.

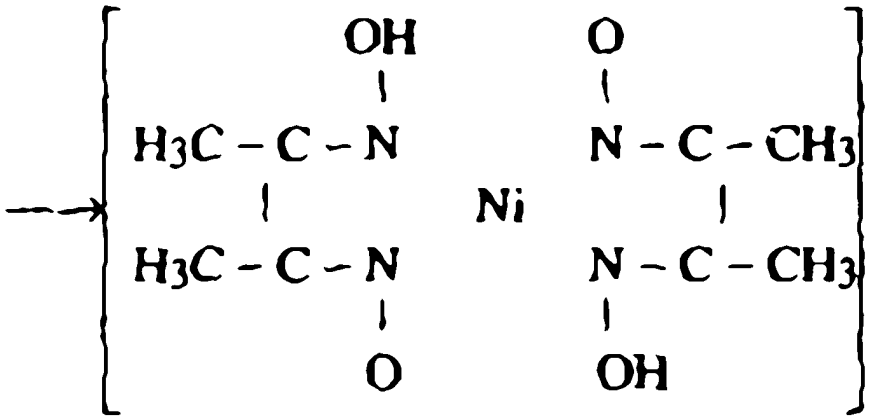
$$Br_2 + H_2O \dashrightarrow 2HBr + O$$

$$2Ni(OH)_2 + H_2O + O \dashrightarrow 2Ni(OH)_3$$

Black ppt.

(ii) Dimethyl Glyoxime Test :

$$NiCl_2 + 2NH_4OH + 2 \begin{array}{l} CH_3 - C = NOH \\ | \\ CH_3 - C = NOH \end{array}$$



Bright red complex

Manganese (Mn^{2+}) : Manganese sulphide dissolves in dilute HCl to form manganese chloride and H_2S is boiled off.

$$MnS + 2HCl \longrightarrow MnCl_2 + H_2S\uparrow$$

(i) PbO_2 Test :

$$MnS + 2HNO_3 \longrightarrow Mn(NO_3)_2 + H_2S$$

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \longrightarrow$$

$$2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O$$

Pink Solution

(ii) NaOH and Br_2 Water Test :

$$MnCl_2 + 2NaOH \longrightarrow \underset{\text{White ppt.}}{Mn(OH)_2} + 2NaCl$$

$$Br_2 + H_2O \longrightarrow 2HBr + [O]$$

$$Mn(OH)_2 + [O] \longrightarrow \underset{\text{Brown ppt.}}{MnO(OH)_2}$$

Zinc (Zn^{2+}) :

$$ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S \uparrow$$

(i) NaOH Test :

$$ZnCl_2 + 2NaOH \longrightarrow \underset{\text{White ppt.}}{Zn(OH)_2} + 2NaCl$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Soluble}}{Na_2ZnO_2} + 2H_2O$$

(ii) Potassium Ferrocyanide Test :

$$2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{White or Bluish white ppt.}}{Zn_2[Fe(CN)_6]} + 4KCl$$

Reactions Involved in Group V Analysis :

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3\downarrow + 2NH_4Cl$$

$$SrCl_2 + (NH_4)_2CO_3 \rightarrow SrCO_3\downarrow + 2NH_4Cl$$

$$BaCl_2 + (NH_4)_2CO_3 \rightarrow BaCO_3\downarrow + 2NH_4Cl$$

These insoluble carbonates dissolve in acetic acid and form soluble acetates.

Calcium (Ca^{2+}) : White ppt. of $CaCO_3$ is dissolved in hot dilute acetic acid

$$CaCO_3 + 2CH_3COOH \longrightarrow$$

$$(CH_3COO)_2Ca + CO_2\uparrow + H_2O$$

(i) Ammonium Oxalate Test

$$(CH_3COO)_2Ca + (NH_4)_2C_2O_4 \longrightarrow$$

$$2CH_3COONH_4 + \underset{\text{White ppt.}}{CaC_2O_4}$$

(ii) Flame Test : Calcium imparts brick red colour to the flame.

Strontium (Sr^{2+}) : White precipitate of $SrCO_3$ is dissolved in hot dilute acetic acid.

$$SrCO_3 + 2CH_3COOH \longrightarrow$$

$$(CH_3COO)_2Sr + CO_2\uparrow + H_2O$$

(i) Ammonium Sulphate Test :

$$(CH_3COO)_2Sr + (NH_4)_2SO_4 \longrightarrow$$

$$SrSO_4\downarrow + 2CH_3COONH_4$$

White ppt.

(ii) Flame Test : Strontium imparts crimson red colour to the flame.

Barium (Ba^{++}) : White precipitate of $BaCO_3$ is dissolved in hot dilute acetic acid.

$$BaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ba$$

$$+ CO_2\uparrow + H_2O$$

(i) Potassium Chromate Test :

$$(CH_3COO)_2Ba + K_2CrO_4 \longrightarrow \underset{\text{Yellow ppt.}}{BaCrO_4\downarrow} + 2CH_3COOK$$

(ii) Flame Test : Barium produces grassy green colour to the flame.

Reactions Involved in Group VI Analysis :

Ammonium (NH_4^+) :

$$NH_4Cl + NaOH \longrightarrow NH_3\uparrow + NaCl + H_2O$$

Nessler's Reagent Test :

$$\underset{\text{Nessler's Reagent}}{2K_2HgI_4} + NH_3 + 3KOH \longrightarrow H_2N.HgO.HgI + 7KI + 2H_2O$$

Magnesium (Mg^{2+}) :

Ammonium Phosphate Test :

$$MgCl_2 + NH_4OH + (NH_4)_2HPO_4 \longrightarrow$$

$$Mg(NH_4)PO_4\downarrow + 2NH_4Cl + H_2O$$

White ppt.

Sodium (Na^+) :

Potassium Pyroantimonate Test :

$$2NaCl + K_2H_2Sb_2O_7 \longrightarrow Na_2H_2Sb_2O_7 + 2KCl$$

Potassium Pyroantimonate — Sod. Pyroantimonate Milkyness or ppt.

Potasium (K^+) :

(i) Picric Acid Test :

$$KCl + C_6H_2(NO_2)_3OH \rightarrow C_6H_2(NO_2)_3OK + HCl$$

Picric acid — Pot. Picrate Yellow ppt.

(ii) Sodium Cobaltinitrite Test :

$$3KCl + Na_3[Co(NO_2)_6] \longrightarrow K_3[Co(NO_2)_6] + 3NaCl$$

Pot. cobalt nitrite Yellow ppt.

APPENDIX I

Some of the important SI units are listed in the following table :

Quantity	Name of Unit	Symbol of Unit	Definition of Units
Length	metre	m	—
Mass	kilogram	kg	—
Time	second	*s*	—
Temperature	kelvin	K	—
Amount of substance	mole	mol	—
Electric current	ampere	A	—

Energy	joule	J	$kg\ m^2\ s^{-2}$
Force	newton	N	$kg\ ms^{-2} = Jm^{-1}$
Pressure	Pascal	Pa	$kg\ m^{-1}\ s^{-2} = Nm^{-2}$
Electric charge	coulomb	C	As
Electric potential difference	volt	V	$Kg\ m^2\ s^{-3}\ A^{-1}$ $= JA^{-1}\ s^{-1}$
Electric resistance	ohm	Ω	VA^{-1}
Electric capacitance	farad	F	$As\ V^{-1}$

APPENDIX II

Some Important Physical and Constants		
Quantity	**Symbol**	**Value**
Avogadro's number	No	$6.0222 \times 10^{23}\ mol^{-1}$
Boltzmann constant	k	$1.30062 \times 10^{-23}\ JK^{-1}$
Gas constant	$R = N_aK$	$8.3143\ JK^{-1}\ mol^{-1}$
Atmospheric pressure	P	$1atm = 101325\ Nm^{-2}$

Absolute Temperature	T_o	OK
Faraday	F	$96490\ C\ mol^{-1}$
Velocity of light	C	$2.997925 \times 10^{8}\ ms^{-1}$
Mass of electron	m	$0.91096 \times 10^{-30}\ kg$
Charge on electron	e	$1.6021 \times 10^{-19}\ C$
Planck's constant	h	$6.6230 \times 10^{-34}\ Js^{-1}$

APPENDIX III

Table of Amino Acid

Name	Formula	Molecular weight
Glycine	$CH_2(NH_2).COOH$	75.1
Alanine	$CH_3CH.(NH_2).COOH$	89.1
Phenyl-alanine	$C_6H_5CH_2CH.(NH_2).COOH$	165.2
Tyrosine	$C_6H_4OH.CH_2CH.(NH_2).COOH$	181.2

Name	Formula	Molecular weight
Valine	$(CH_3)_2CH.CH.(NH_2).COOH$	117.1
Leucine	$(CH_3)_2CH.CH_2CH.(NH_2).COOH$	131.2
Iso-leucine	$(CH_3).CH_2CH(CH_3)CH.(NH_2).COOH$	131.2
Serine	$CH_2OH.CH.(NH_2).COOH$	105.1
Threonine	$CH_3CHOH.CH.(NH_2).COOH$	119.1
Cysteine	$SH.CH_2CH.(NH_2).COOH$	121.1

Name	Formula	Molecular weight
Cystine	$[HOOC.CH(NH_2)CH_2S]_2$	240.3
Methionine	$CH_3S.(CH_2)_2CH.(NH_2).COOH$	149.2
Asparagine	$NH_2CO.CH_2CH.(NH_2).COOH$	132.1
Glutamine	$NH_2CH.(CH_2)_2(CO.NH_2).COOH$	146.1
Lysine	$NH_2(CH_2)_4CH.(NH_2).COOH$	146.2
Arginine	$NH_2C(:NH).NH(CH_2)_3CH.(NH_2).COOH$	174.2

Name	Formula	Molecular weight
Aspartic	$COOH.CH_2CH.(NH_2).COOH$	133.1
Glutamic	$COOH.(CH_2)_2CH.(NH_2).COOH$	147.1
Histidine	$C_3H_3N_2.CH_2CH.(NH_2).COOH$	155.2
Tryptophan	$C_6H_4.NH.C_2H.CH_2CH.(NH_2).COOH$	204.2
Proline	$NH.(CH_2)_3CH.COOH$	115.1

APPENDIX IV

Minerals of some Metals

Metal	Minerals with their chemical formulae
Ag	Silver glance—Ag_2S
	Horn silver—AgCl
	Native silver
Al	Bauxite—$Al_2O_3.2H_2O$
	Cryolite—$3NaF.AlF_3$
Au	Native gold

Metal	Minerals with their chemical formulae
Ca	Limestone—$CaCO_3$
	Dolomite—$CaCO_3.MgCO_3$
	Gypsum—$CaSO_4.2H_2O$
Cu	Copper pyrites—$Cu_2S.Fe_2S_3$
	Copper glance—Cu_2S
	Malachite—$CuCO_3.Cu(OH)_2$
Cr	Chromite—$FeO.Cr_2O_3$

Metal	Minerals with their chemical formulae
Fe	Haematite—Fe_2O_3
	Magnetite—Fe_3O_4
	Iron pyrites—FeS_2
Hg	Cinnabar—Hgs
K	Sylvine—KCl
	Carnallite—$KCl.MgCl_26H_2O$
	Felspar—$K_2O.Al_2O_3.6SiO_2$
Mg	Magnesite—$MgCO_3$

Metal	Minerals with their chemical formulae
Mg	Dolomite—$CaCO_3.MgCO_3$
	Carnallite—$KCl.MgCl_2 6H_2O$
Mn	Pyrolusite—MnO_2
Na	Rock salt—NaCl
	Chile salt petre—$NaNO_3$
Na	Borax—$Na_2B_4O_7.10H_2O$
Ni	Nickel glance, NiAsS
Pb	Galena—Pbs

Metal	Minerals with their chemical formulae
Sn	Tinstone—SnO_2
Sb	Stibnite—Sb_2S_3
Ti	Rutile—TiO_2
	Ilmenite—$FeO.TiO_2$
Zn	Zinc blende—Zns
	Zincite—ZnO
	Calamine—$ZnCO_3$

Letters		Names
A	α	alpha
B	β	beta
Γ	γ	gamma
Δ	δ	delta
E	ε	epsilon
Z	ζ	zeta
H	η	eta
Θ	θ	theta

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